AN INVESTIGATION OF THE BASE EXCHANGE PROPERTIES OF CERTAIN CLAY MINERALS

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An Investigation of the Base Exchange Properties of Certain Clay Minerals

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INTRODUCTION

This thesis is part of a series of related investigations concerning the properties of clay being carried out by the Soil Mechanics Department of Rensselaer Polytechnic Institute. It is the purpose of this thesis to determine the variation of the base exchange capacities of three certain clay minerals with hydrogen ion concentration, and also to attempt by spectrographic analysis to determine both qualitatively and quantitatively the nature of the exchangeable bases present.

The basis for the work concerning base exchange capacity was a series of investigations conducted by J. S. Hosking. We attempted to duplicate his methods and confirm his results, at the same time extending the theory to Illite which he did not investigate.

R. F. Reuss investigated the use of the spectrograph in the identification and classification of clay minerals. With his results as a background we attempted to determine the adsorbed ion content and convert it into terms of base exchange capacity.

PART II

THEORY

A. Theory of the Clay Minerals

B. Theory of Base Exchange

C. Theory of Variation of Base Exchange Capacity with Hydrogen Ion Concentration

D. Theory of the Spectrograph

THEORY

A. Theory of Clay Minerals

The theory of base exchange has been known for well over a century. The first classical work was that of Thomas Way, who, in 1850 published, "The Power of Soil to Absorb Manure". In 1852, Way, in a second paper concluded that base exchange is caused by the clay material of the soil and that this active material is an hydrated alumina silicate. Way's conclusions from his experiments, as modified by various investigators, have stood the test of time.

Before proceeding with a discussion of base exchange, it would be better to first consider the clay minerals themselves. The study of the structure of clay material has been closely associated with base exchange. The clay minerals are crystalline hydrous aluminum silicates produced by weathering of feldspars and other silicates. The crystalline nature of clay was first established by Hendricks and Fry in 1930, and is of major importance.

When ions or molecules combine to form a crystalline solid, they tend to group themselves in a geometrical arrangement which will result in the greatest possible degree of electrical neutralization. The most elementary grouping is called a unit cell, and is the elementary building unit.

For silicon and aluminum, the unit cells are termed the silicon-oxygen tetrahedron and the aluminum-hydroxyl octahedron. These are the principal constituents of the lattices of the various clay minerals. They are bonded together by electrostatic forces, and since the units are not electrically neutral they combine to form the tetrahedral silica sheet and the Gibbsite sheet, respectively

Note that in each case, the surfaces will have unsatisfied negative valences, and as a result will exert an attractive electrostatic force on any atoms or ions in their environment which have an unsatisfied positive valence or charge in an attempt to reduce the surface energy and become electrically neutral. Moreover, the atoms at the end of the sheets will have unsatisfied valences simply because there are no adjacent atoms.

Thus, it is seen that the electrostatic forces exerted by a crystalline particle are due to the unsatisfied charges located in the surfaces, edges, and corners of the particle. These surfaces, edges, and corners are termed structural discontinuities, and it is obvious that the greater the number of discontinuities for a given volume of matter, the more electrostatically active the material will be or the greater the quantity of ions required to be adsorbed to produce neutralization.

In the basis of lattice structure, the clay minerals of major importance may be classified into

three groups: Kaolinite, Montmorillonite and Illite. Each group takes its name from its principal member, and it is with these three that we shall concern ourselves.

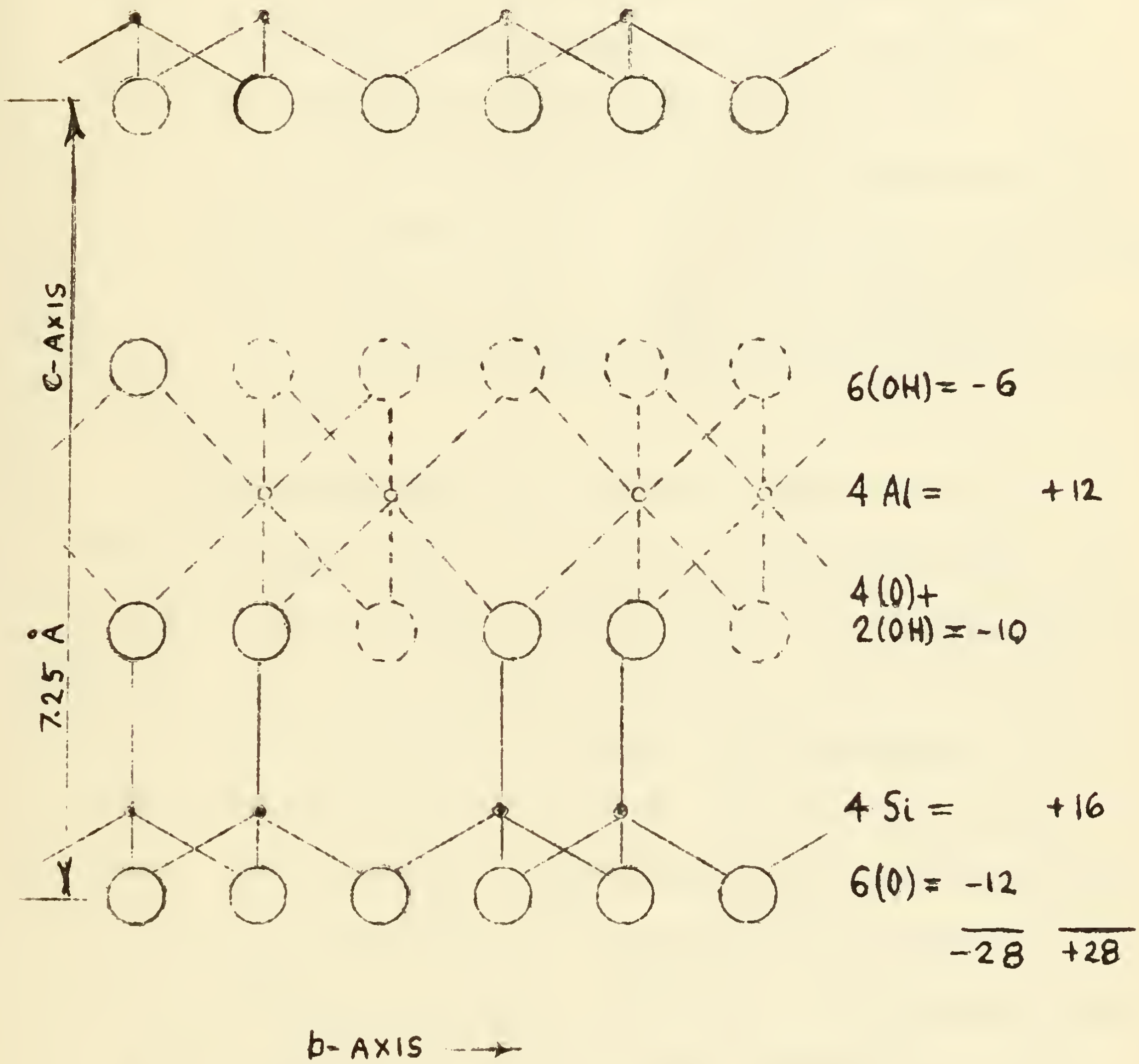
Some soils contain mixtures of the clay minerals but in many soils there is but a single clay which is predominant. These latter are mature soils which have had time for the clay mineral to reach equilibrium in its environment.

Illite is usually a remnant of the decomposition of the parent rock material. Kaolinite and Montmorillonite may form from the same parent rock in a different environment. Montmorillonite and Kaolinite may form from Illite. Kaolinite may form from Montmorillonite but the converse seems to be questionable.

In sediments accumulating on the ocean floor, Illite appears to be the most widely distributed clay mineral. Ancient sedimentary clays are most frequently mixtures of Illite and Kaolinite; occasionally, small amounts of Montmorillonite are present. Many so-called Bentonites formed by alteration of volcanic ash are composed of Montmorillonite.

The composition of Kaolinite is given as $(OH)_8Al_4Si_4O_{10}$. Its lattice (Fig. A) consists of a Gibbsite sheet and a tetrahedral silica sheet, i.e., a 1:1 lattice structure. The charges on the lattice are balanced; therefore, it cannot attract external

KAOLINITE $Al_4Si_4O_{10}(OH)_8$



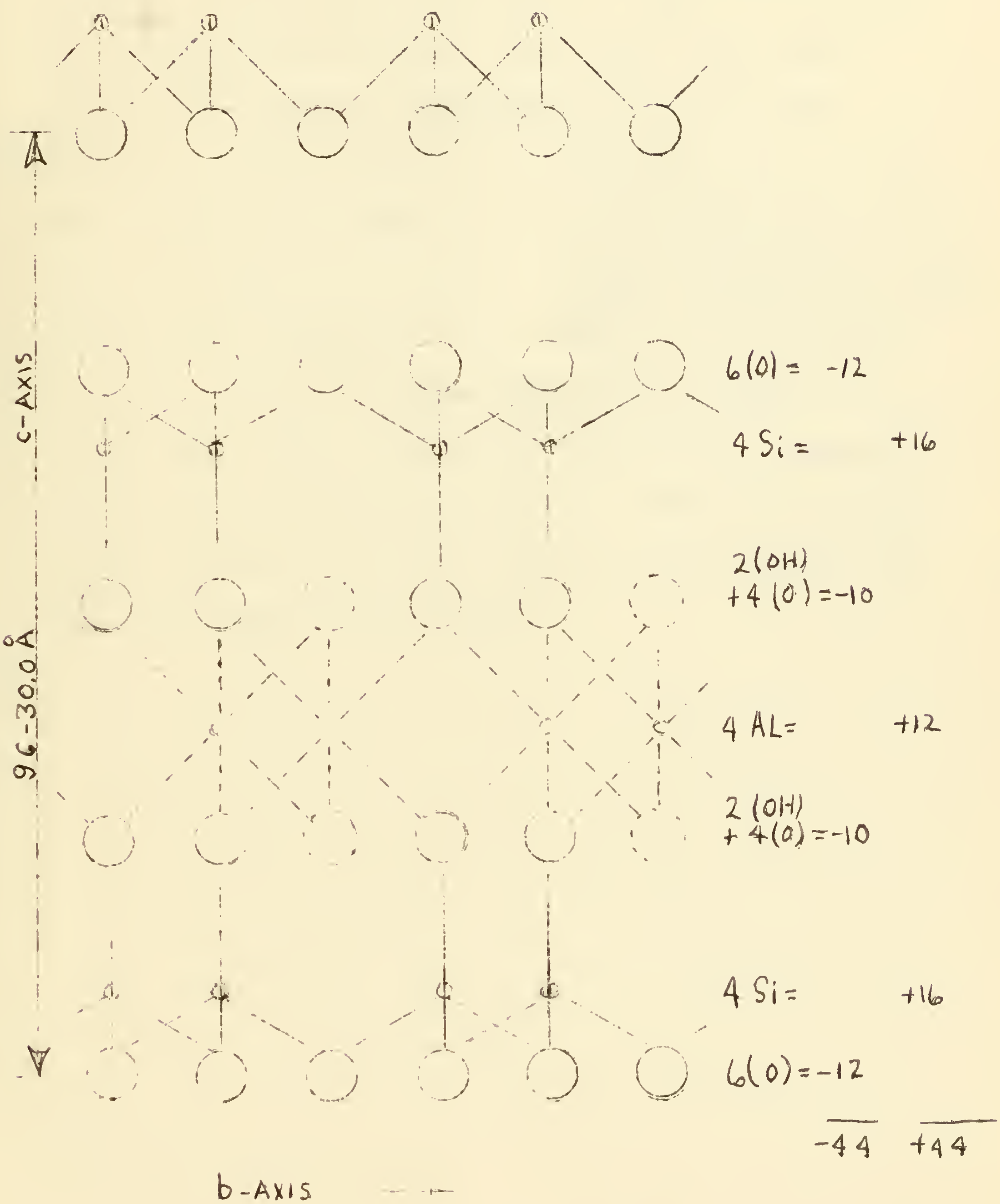
AFTER GRUNER

Fig. A

cations except by the negative charges on the terminal oxygen ions on the lattice edges. Also, the lattice has hydroxyl ions at one basal plane and oxygen on the other, which produces a tight bonding within the lattice and between lattices because of the strong attraction between OH- and O-- ions. As a result, this lattice structure does not expand and its base exchange capacity is very low (3-15 m.e. per 100 gms.). Its exchange capacity will increase with decreasing particle size (greater number of discontinuities produced by broken bond).

Montmorillonite has a probable composition of $(OH)_4Al_4Si_8O_{20}$ x H_2O. Its lattice structure (Fig. B) consists of one Gibbsite sheet between two tetrahedral silica sheets, i.e., a 2:1 lattice structure. This unit has oxygen ions at both basal planes, and therefore, no strong bonding force acts within the unit or between layers. Water dipoles occupy the space between adjacent lattices, and depending on the quantity of water, the lattice spacing will vary. Obviously, the greater number of discontinuities produced by this expanding lattice will greatly increase its base exchange capacity (60-100 m.e. per 100 gms.). Moreover, because of the greater magnitude of surface discontinuities relative to total discontinuities, the base exchange capacity does not vary with particle size.

MONTMORILLONITE $(OH)_4Al_4Si_8O_{20} \cdot nH_2O$

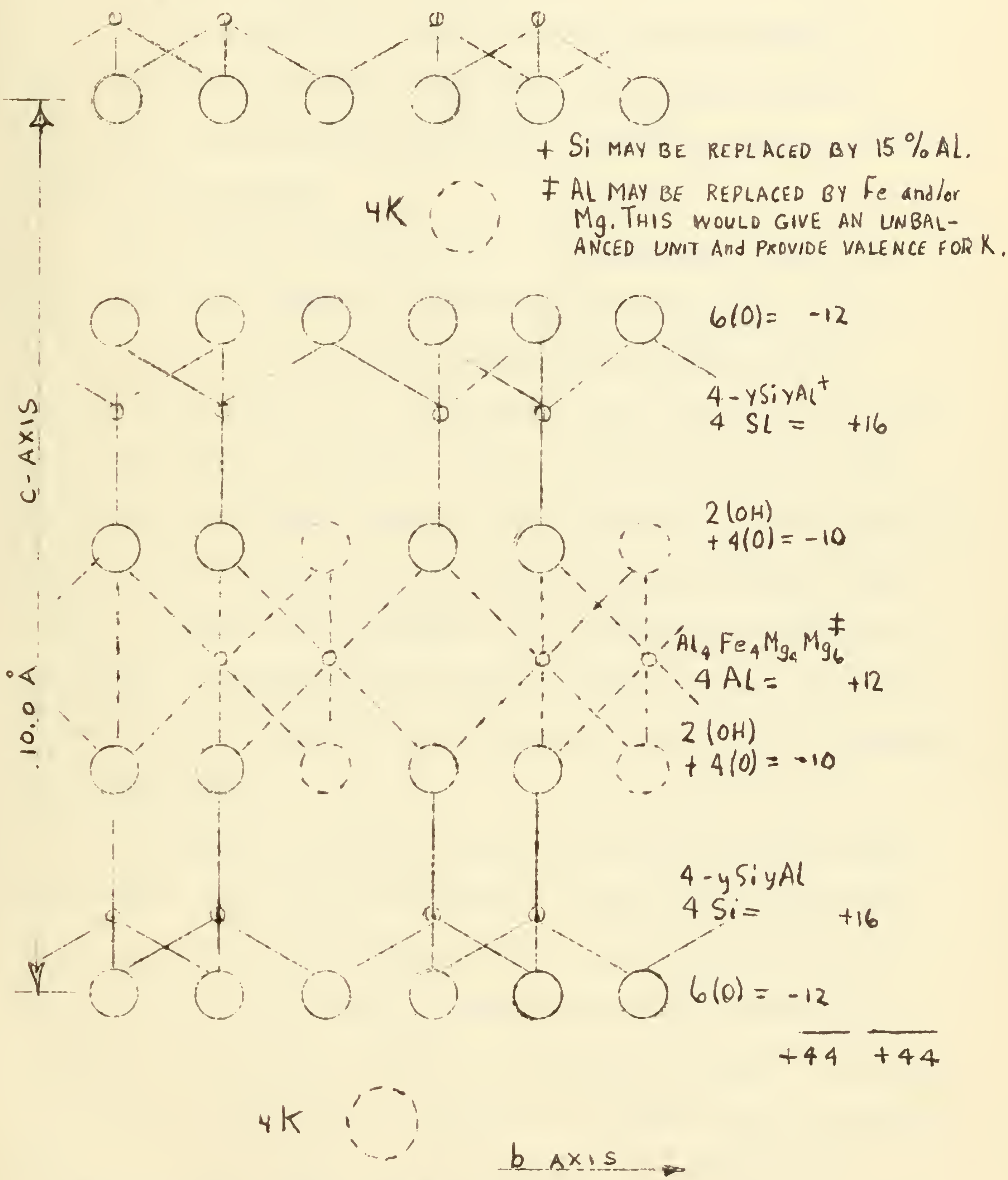


AFTER HOFMANN, ENDELL and WILM

Fig. B

<u>Illite</u> has a probable composition of $(OH)_4K_y(Al_4Fe_4Mg_4Mg_6)Si_{8-y}Al_yO_{20}$, y varying from 1 to 1.5. Its lattice structure (Fig. C) is similar to montmorillonite except that about 15% of the Si++++ positions are replaced by Al+++ and the resulting excess charges are satisfied chiefly by K+ ions between the silica sheets of two adjacent units. These K+ ions seem to act as bridges binding the units together so that they do not expand in the presence of water. Thus, it appears that the properties of Illite will range between the extremes as represented by Kaolinite and Montmorillonite. Its base exchange capacity varies from 20 to 40 m.e. per 100 gms. and will vary with particle size.

ILLITE $(OH)_4\,K_y\,(Al_4\,Fe_4\,Mg_4\,Mg_6)(Si_{8\,y}Al_y)O_{20}$



After Grim, Bray and Bradley

Fig. C

B. THEORY OF BASE EXCHANGE

It has been shown that unsatisfied negative valences exist in the zones of discontinuity. These valences in turn are satisfied by cations which are packed in the interstices of the polyhedrons and held there by the forces (mainly electrostatic) existing between the cations and anions.

Thus, ionic exchange may be visualized as acting in a definite pattern, conforming to Helmholtz double layer theory. The electro-negative framework of O-- and OH- ions acts as an attractive wall (inner layer) for the adsorption of cations. The cations themselves form the outer or diffuse layer. This structural arrangement of the O-- and OH- ions remains undisturbed as long as the + and - changes are balanced. The forces of attraction are mainly electrostatic (except perhaps H+ as explained later) and are greater the closer the cations can approach the oxygen ions.

It follows, therefore, that ions of different size and charge will act differently in their adsorption and release. The relationship between ionic exchange and properties of the ions has been extensively studied in permutits (artificial clays) and natural clays. In using the latter it is first necessary to isolate the colloidal fraction of the sample and subject it to purification processes which will not affect the nature of the colloid.

Then study can be made to obtain quantitative and qualitative evaluation of the mechanism of ionic exchange.

Ionic exchange varies in intensity with the cation studied, and the individual behavior of various ions is manifested through a range of concentration. It has been found that there is a systematic trend in regard to the cation used, i.e., a definite lyotropic series exists. Moreover, this series exists for both adsorption and release of ions in reverse order.

In permutit systems the adsorption series is as follows:

$$Li < Na < K < Rb < Cs < H$$

Except for hydrogen, these ions are arranged according to their atomic weights and then crystal lattice radii. Thus, it would appear that the smaller the radius of the ion the less the adsorption.

This statement, however, appears to be directly opposite to what one would expect from analogies of attraction and energy relations of crystal lattices. According to various investigators, the attraction between anions and cations follows Coulomb's Law which demands that for cations of equal charge a small ion will be attracted with greater force and held more tightly than a large ion. This is expressed as follows:

$$\frac{e_a \cdot e_c}{(r_a + r_c)^2}$$ where e is the charge and r is the radius

of the cation and anion as indicated. It is evident from the denominator that attraction and stability are greater the smaller the radii of the ions. Thus, it appears that in ionic exchange the cations apparently act contrary to Coulomb's Law.

For an explanation of this, it seems logical to attribute the order of the lyotropic series to the phenomenon of hydration of ions. Water molecules which are permanent dipoles become oriented and attracted, turning their negative side toward the cation. The number of polarized water molecules increases with the polarizing ability of the ion, which is stronger the greater its charge and the smaller its radius. The small Li ion will, therefore, attract the most water molecules and the large Cs ion the least. Thus, the Li ion will then be the largest ion and Cs the smallest as based on radii of hydration. Therefore, the apparent reverse of Coulomb's Law does not exist at all and ionic exchange does follow that law, and its mechanism is easily visualized.

The strongly hydrated, large, and voluminous Li ion cannot come very close to the negative oxygen ion of the crystal lattice. Since there are one or two water molecules between the colloidal particle and the adsorbed ion, the forces of attraction are weak and are more easily replaced by less hydrated and, consequently, smaller ions.

In natural clays there are irregularities in the lyotropic series; e.g., for bentonite adsorption:

$Na < K \leqq Li < H$

This may be interpreted as resulting from the reversal of the normal hydration order of the exchanging cations, i.e., there exists a marked tendency to reverse the normal lyotropic series.

In the proceeding discussion, the hydrogen ion was not mentioned because of its peculiar behavior. It is unquestionably the best adsorbed ion and is most effective in replacing other cations.

The hydrogen ion consists of only a positive nucleus and is the smallest ion known. From analogy from before, it should be the least adsorbed cation rather than the best.

This strong adsorption and release is perhaps better understood from a consideration of the forces of attraction. The bonds existing between the oxygen ion framework and the adsorbed cations are considered to be of mere electrostatic nature. The adsorbed H-ion naturally tends to form OH^- ions and even H_2O molecules with O^{--} ions of the lattice. This attraction between H^+ and O^{--} is very great, and the two ions adhere so closely that the H ion plunges into the electron orbits of the oxygen ion. This bond may be considered to be of the covalent type, i.e., the two ions share two electrons simultaneously. This type bond represents true chemical linkage most closely.

Thus, the difference in type bond seems to explain the action of the H-ion. In the case of Li where at least one water molecule stands between the O-- and the cation, the attraction is weak and electrostatic in nature, while for H+ the forces are strong and seem to be of a true chemical type.

Investigations on the water adsorption of soil colloids by various methods show decidedly that the hydration of the colloid particles depends upon the nature of the adsorbed cation.

A crystal lattice contains large cavities which are filled with adsorbed ions and water molecules. For a given lattice the number of water molecules which can be packed into one cavity apparently depends on the number and size of the exchangeable ions within the cavity. The smaller the number and size of the adsorbed ions, the greater will be the number of water molecules in the system.

In monovalent systems for every cation adsorbed, another is released. The number of water molecules within the cavities becomes dependent only upon the size of the adsorbed cation. The smaller the cation in the cavity, the greater the number of water molecules that can be packed into the system.

In divalent systems, for every divalent cation adsorbed, two monovalent cations are released. Although the entire system remains electrically balanced, the place of one of the two cations remains unoccupied.

For instance, the volume of two Na ions is 7.88 A^3, while the volume of one Ca ion, which replaces the two Na ions, is only 4.99 A^3. This differential space can be filled with water molecules. Thus, it follows that systems with divalent cations are more hydrated than those with monovalent cations.

It follows from above that H systems should contain the most water of hydration, since the H-ion is the smallest ion of all. Data further indicates that the number of water molecules in H-systems is considerably greater than that provided by mere space relationships. Jenny states that this additional water represents water of constitution formed during the process of replacement. Because of the framework of oxygen and hydroxyl ions, the replacement of cations by H-ions creates "potential water molecules" which are liberated upon ignition of the new compound.

Thus, the hydration of H-systems may be visualized as consisting of two main parts: first the ordinary water of hydration (water films around the colloidal particles and cavity water) and second, the water of constitution.

C. THEORY OF VARIATION OF BASE EXCHANGE CAPACITY WITH HYDROGEN ION CONCENTRATION

Materials such as clay minerals and complex organic compounds, in soils capable of exhibiting the property of cation exchange, are in reality weak multibasic acids in which the hydrogen ions are distributed over the exposed surfaces of large insoluble anions. These hydrogen ions may be wholly or in part replaced by metallic cations. Since these exchange materials are weak acids, complete neutralization of the hydrogen ions capable of dissociation will not take place at the neutral point, pH 7, but at a more alkaline reaction, the equivalence point.

In practice the equivalence point of the clay minerals is extremely difficult, if not impossible, to determine. As a result, various reaction values have been adopted as standard reference points at which to express saturation or cation exchange capacity. Of these values two, pH 7 and pH 8.4 have a special, though not necessarily a fundamental significance. The neutral point, pH 7, is of agronomic importance and the determination of the capacity at this value is based upon a desire for information concerning the lime required to neutralize an acid soil; pH 8.4 is of pedological importance since free calcium carbonate may appear in the soil at this pH value.

In the past the majority of American workers adopted pH 7 as the standard of reference. Bradfield and Allison (1933) proposed pH 8.4 as a more logical reference point. They based their proposal upon the observation that in most soils of the humid regions calcium is the dominant exchangeable cation, and that in such soils it might be expected that the pH value would not normally rise appreciably above 8.4 (the pH of calcium carbonate in equilibrium with carbon dioxide), since any metallic cations in excess of the amount necessary to neutralize the exchange complex to this value would appear as calcium carbonate.

However, the reaction value rises appreciably above pH 8.4 in soils containing either magnesium or sodium as the dominant or an important exchange cation; this is quite normal not only in arid regions, but also in humid regions and frequently even in the lower horizons of soils with calcium as the principal exchangeable ion in the surface layers.

It is evident that there is a necessity for agreement among investigators as to a definition of cation exchange capacity as well as to a method for its determination.

Hosking attempted to solve these problems through extensive investigation. From his results he determined that the most logical reference point for the

characterization and comparison of the exchange capacities of soils is pH 9. He found for all his samples that the cation exchange capacities increased from a minimum value at pH 5 to a maximum value at pH 9. He recommends that the term "maximum cation exchange capacity" should be used for the value at pH 9 and that for the comparison of the exchange capacities of soils and colloids this maximum value should be used.

While such a point is of fundamental importance, a value of more practical significance so far as each individual soil is concerned is its exchange capacity at its own pH value. This value is a definite characteristic of the soil as it occurs in its natural state. Since, however, any treatment in the field will necessarily upset the balance in the extent and nature of the exchangeable cations present, and must result in some variation in the pH value, the pH of the soil may become somewhat transient, in the surface layers at least, under cultivation, and a knowledge of the likely variation in cation exchange capacity with change in pH is essential.

The method employed by Hosking is described (modifications noted) in the Procedure. It may be used to determine, in a single operation, exchange capacity of soils over the useful range from pH 5 to 9 and beyond this for mineral samples. It has the advantage over other methods in that only small samples (as low as 0.1 to 0.5 g) may be used where material is restricted and is relatively rapid.

D. THE SPECTROGRAPH

By supplying energy to the atoms of an element in the form of heat and other methods, the electrons in the outer shells or orbits are displaced to levels of higher energy creating what may be termed an "excited" state of the atom. These "excited" atoms are unstable and tend to return to normal emitting their surplus energy in the form of light. The light thus emitted is made up of discreet wavelengths which are characteristic of the element and range from the far ultra-violet to the infra-red, (1500A° - 7500A°). In general, this process is not greatly altered by chemical combination, each element in a compound emitting its own characteristic spectra of wavelengths.

If the light emitted by a particular group of elements is dispersed by some means such as a grating or a prism, the individual wavelengths may be recorded on a photographic plate and identified. As the amount of an element in the source becomes very small, their ultimately remain only a very few lines of its spectrum. These lines will always be the last to disappear and will disappear in the same order. They are known as the "persistent lines".

It follows that in qualitative analysis for an element, if the persistent lines are absent, that element is not present in the sample. For quantitative

analysis, the amount of each element present will determine the relative intensities of its spectral lines on the plate. The measure of the intensities can be made by the use of a densitometer.

In order to determine the adsorbed ion content of a material such as the clay minerals investigated it is necessary to analyze qualitatively and quantitatively samples of the material before and after treatment to remove the adsorbed ions. The difference in amount present in the samples should total the adsorbed ion content.

Part III

MATERIALS AND APPARATUS

Materials and Apparatus

The three certain clay minerals used in this investigation are as follows:

KAOLINITE-from Dry Branch, Georgia

GRUNDITE-an Illite bearing shale from Joliet, Ill.

BENTONITE-from Wyoming

The equipment used for base exchange capacity determinations is as follows:

Centrifuge-Size 1, Type C (International Equip. Co.)

Roller Particle Size Analyzer (American Inst. Co.)

Kjeldahl Distillation Apparatus

The three standard clays used in the spectrographic work for the plotting of the working curves as explained in the Procedure are as follows:

KAOLINITE-from Macon Georgia (H-4)

ILLITE-from Fithian, Ill. (H-35

BENTONITE-from Clay Spur, Wyoming (H-26)

These standard clay minerals have been collected and identified by the American Petroleum Institute.

The spectrographic equipment used is as follows:

Leeds and Northrup Densitometer, Cat. No. 6700-P

Leeds and Northrup Speedomax Recorder

Baird Associate s Grating Spectrograph

Photo #1 Kjeldahl Apparatus

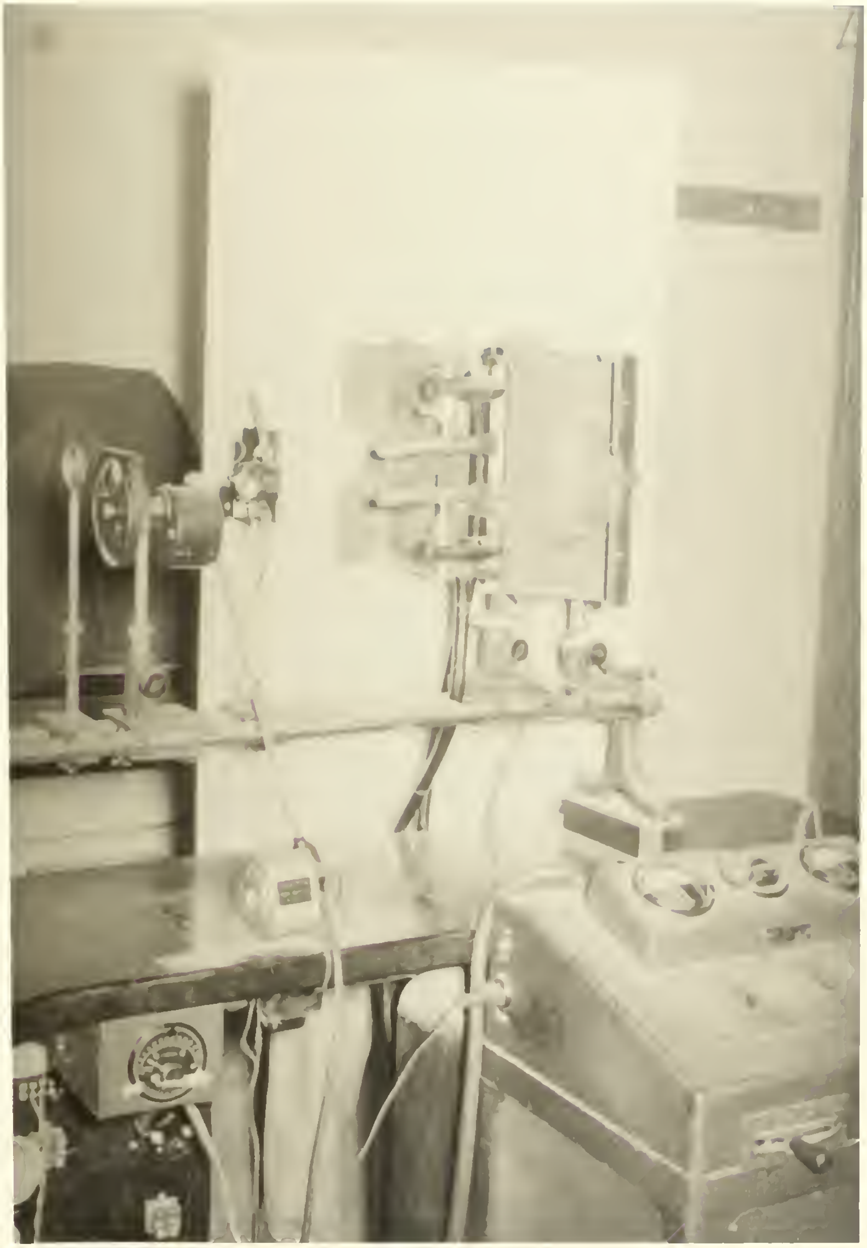


Photo # 2 Electrodes, Holder, and Controller.

Photo #3 The Spectrograph

Photo # 4 The Densitometer

Photo #5 Densitometer Recorder

Part IV

PROCEDURE

A. Preparation of Samples for Base Exchange Capacity Determinations

B. Determination of Organic Matter in Clay Samples

C. Spectrographic Analysis

Preparation of Sample for the Determination of Base Exchange Capacity

Soil in the natural state generally consists of both cohesive and non-cohesive fractions. It is the former, often broadly referred to as clay with which we are concerned. This clay fraction is further divided by particle size. Below 2 microns (u) a definite change in physical properties is observed. This fraction $<$ 2 u is called the "active fraction".

Since particle size influences the activity, it was decided to run all tests on a given particle size. The choice of size resulted from several considerations. Atterberg states the 2 u particles exhibit a definite change in properties; a distinct change in physical properties and commencement of Brownian Movement. It was thought unwise to set merely an upper limit, since the gradation of smaller sizes would be unknown. Considering both these views, the fraction 1-3 u was selected. If subsequent investigators use this same fraction, the comparative results will be more meaningful and should be closely duplicated.

The presence of organic matter affects the base exchange capacity, and the procedure followed in its determination differs for clays with and without organic matter. Each type--Wyoming Bentonite, Georgia Kaolin and the Illite bond clay was in turn saturated with hydrogen peroxide and then dried to ascertain

any weight change which would indicate oxidation of organic matter. Negative results were found on all three types, thus permitting identical procedures for base exchange capacity determinations.

Stoke's Law was applied to separate the desired particle size. He stated, "the resistance offered by liquid to the fall of the particle varies with the radius of the sphere and not with the surface." According to the formula:

$$V = \frac{2\ (dp-d)\ g\ r^2}{9\ \eta}$$

V velocity of fall in cm./sec.
g acceleration due to gravity in cm./sec.^{2}
dp density of particle in gm./c.c.
d density of liquid in gm./c.c.
η viscosity of liquid in millipoises

Several inherent limitations of Stoke's Law should be discussed. Clay particles are flat disc-shaped particles rather than spherical. The density is another factor affecting the accuracy of the law. The different mineralogical and chemical composition of the feldspars and micas result in density variations of 2.55-2.75. The generally accepted value of 2.65 was used in our mechanical analysis. Baver emphasizes that it is essential to note that the density of clay particles decreases with particle size when determined in aqueous suspension. This is due to the higher hydration of the smaller particles.

Three methods were used to isolate the sample

fractions, all of which are based on Stoke's Law: sedimentation, centrifugation, and air suspension. Each will be discussed separately.

The Illite bond clay was separated by successive sedimentation. As-received material was sieved and the material passing #200 mesh was retained. The time required for a 3 u particle to settle a given depth was calculated. The material was dispersed in distilled water with a high speed mixer for ten minutes. Sodium oxalate was added as a deflocculating agent as recommended by Baver. This mixture was poured into a plastic cylinder and allowed to settle for the given time. After that period had elapsed, the suspension above the given depth was decanted. It contained particles $<$ 3 u. This suspension was allowed to settle again, for a time sufficient for particles of 1 u to fall a given distance. The suspension above this depth was decanted and discarded as it included particles $<$ 1 u. The sediment (of the desired 1-3 u size) was dried and retained for test.

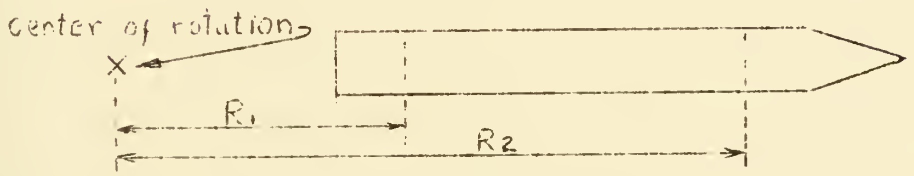
The Georgia Kaolin was separated by centrifugation. The centrifugal force exerted per unit mass upon a given particle depends upon the distance of the particle from the axis of rotation. This is expressed by the relation:

$$\text{Centrifugal Force} = \frac{\text{linear velocity}^2}{\text{radius of rotation}} \quad \text{or} \quad \frac{V^2}{R}$$

This fundamental equation was modified by Steele and Bradfield to:

$$t = \frac{\eta \quad \log \frac{R_2}{R_1}}{3.81 \quad N^2 \quad r^2 \quad (d\ p-d)}$$

η	viscosity in poises
R_2, R_1	measurements of centrifuge tube in cm.
N	revolutions per second
r	radius of particle in cm.
dp-d	densities of liquid and particle, in gm./c.c.
t	time in sec.



Successive centrifugation was employed. The time and speed of rotation were determined for particles of 3 u to settle a definite depth equal to (R_2-R_1). The suspension was then decanted for another centrifuging. The time and speed was recalculated for particles $>$ 1 u to settle. The sediment collected after the second centrifuging was retained and dried as sample. The centrifuge used was Size 1, Type C. Inter. Equip. Co.

The Wyoming Bentonite fraction was isolated by use of the Roller Particle Analyzer. Stoke's Law may be directly applied to the air flow required to raise a particle of a given size. The relationship between

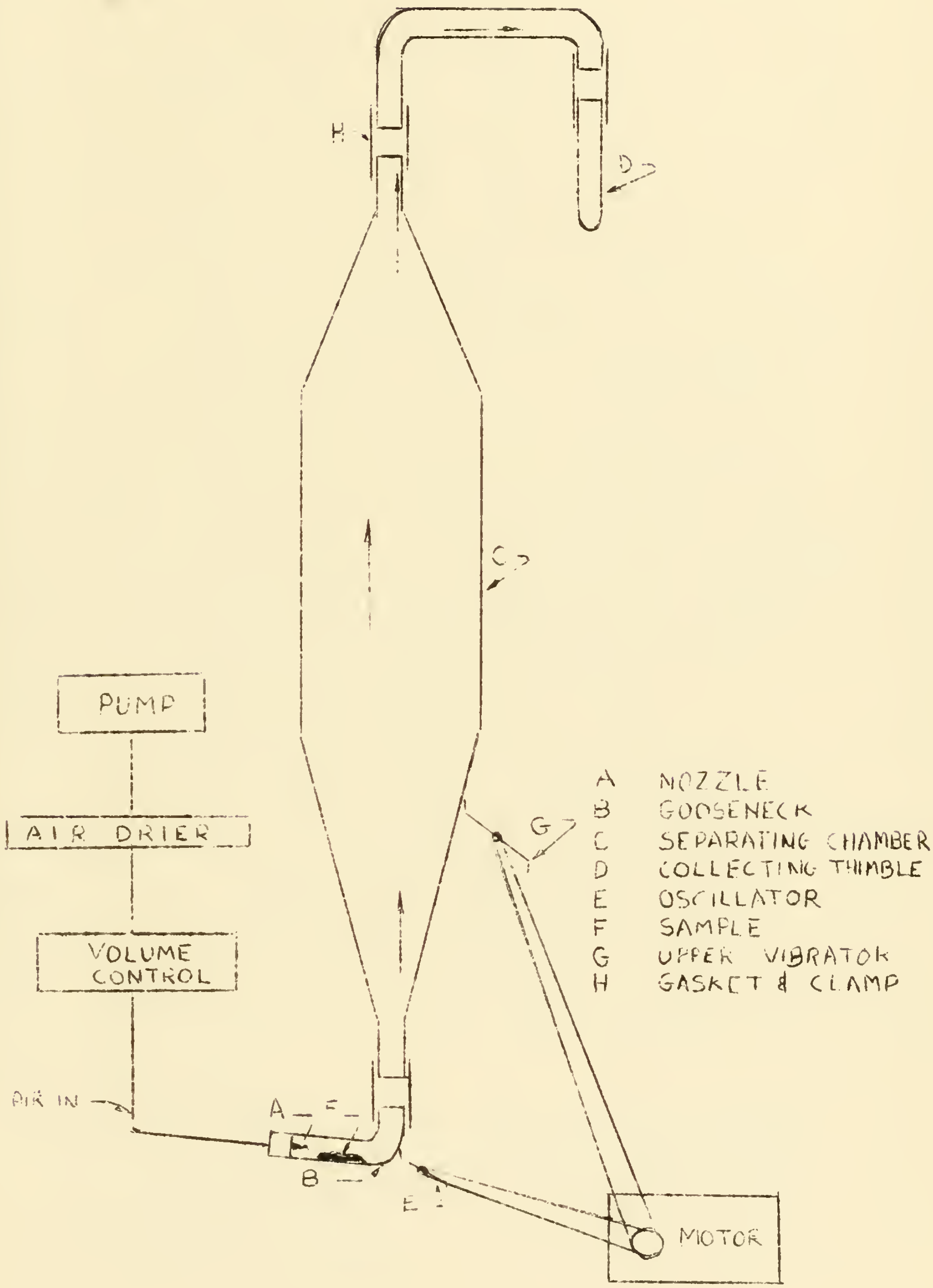
densities of air, particle, and air velocity only need be known.

This principle was incorporated in the development of the Analyzer. This apparatus is used by the Powdered Metallurgy Laboratory and was graciously loaned by that department. The principle employed is merely that a given air flow will just support a certain critical particle size; all smaller particles rising. The as-received material was hand ground and sieved. The portion passing #200 mesh was retained and fed through the Roller Analyzer for segregation of particle sizes < 3 u. Since Jenny states that the base exchange capacity of Montmorillonite does not vary with particle size, it was felt that it would be unnecessary to isolate the 1-3 u fraction, and that the < 3 u fraction would be satisfactory for a comparative analysis with the two other clay minerals investigated.

<u>Preparation of Mixed Sample</u>

A mixed sample was prepared for BEC determinations. Equal parts by weight were taken of KAOLIN, ILLITE, and BENTONITE. They were thoroughly mixed by hammer and pestle. The sample was then stored in the oven at 105°, to await test procedure identical to that used on each of the clay types individually. The BEC was determined at pH 9, the value at which each of the three types indicated a maximum BEC.

SCHEMATIC DIAGRAM of ROLLER ANALYZER



BUILT BY AMERICAN INSTRUMENT CO.
SILVER SPRING, MD.

Procedure

Perhaps the most widely used method for the determination of total base exchange capacity is that of ammonia distillation. The U. S. Bureau of Public Roads adopted a procedure basically identical to the procedure outlined below. The characteristics of the primary reagent used must conform to several patterns. First the attractive forces of the ammonia must be sufficiently great to interchange with those ions originally attached: although ammonia is at the weak end of the lyotropic series, this is accomplished by lengthy and repeated saturation by ammonium acetate. Once attached, ammonia is easily disassociated from the colloid by distillation. The final step consists of titration with an acid to neutralize the ammonia. The quantity required is a direct measure of the colloid's base exchange capacity.

J. S. Hosking, M.Sc., Ph.D., used the procedure as outlined in Ref. 1 to determine the cation exchange capacity of soil colloids with variation of hydrogen ion concentration; the following procedure was modified to use boric acid in step 6 and titration in step 7 was taken from text mentioned.

1. Weigh oven dried sample (105°C) 0.10-1.00 gm. The subsequent filtrations are expedited by using small samples.

2. Saturate the sample with the ammonia ion.

   Add 22.5 ml. of ammonium acetate at desired pH; cap and shake vigorously. Place in water bath of 60°-70°C for two hours--shaking every 15 minutes. Remove from bath. Allow bottle and contents to stand over night.

   Filter suspension through Buchner funnel fitted with 4.25 cm. Whatman #44 filter paper (moisten with same solution as leachate), using slight suction by aid of aspirator. Rinse bottle and cap with leachate until no sample remains. Continue leaching with 5-10 ml. portions of solution until total leachate of 100 ml. is collected. Sample should be allowed to drain completely between each addition.

3. Leachate may now be examined to determine exchangeable bases. This chemical process is long and complicated; spectroscopic analysis may be substituted with no sacrifice of accuracy.

4. Excess ammonia (unattached) is washed off with alcohol. Leach with 5-10 ml. portions of 60% alcohol, washing down material adhering to sides of filter. A total of 50 ml. is sufficient. Finally rinse sample with two lots of 5 ml. 95% alcohol. Allow to dry.

Avoid prolonged exposure to air or some ammonia will be lost.

5. Transfer sample into Kjeldahl Distillation Apparatus. Direct transfer of sample into distilling flask is difficult. It is advisable to transfer sample and paper into a small beaker from which both are carefully washed into the flask. Rinse beaker completely with distilled water, and then continue until sample is diluted by a total of 250 ml. Place 10 ml. of 0.1 N HCl in flask to prevent any loss of ammonia as it stands in flask. If no organic matter is present, add 25 ml. of 1.0 N NaOH to the flask. (0.5 gm. of MgO if organic matter is present).

Two glass beads are inserted to reduce "bumping" as gas becomes superheated.

6. Distillation in Kjeldahl Apparatus. Contents of flask is distilled into 50 ml. of boric acid solution. Distillation continues until 250 ml. of distillate is collected. Practically all ammonia has been disassociated by this time.

7. Titration for determination of total base exchange capacity. (from Standard Methods for the Examination of Water and Sewage; published by the American Public Health Association p. 118-119).

Reagents: Boric acid solution.

Dissolve 40 gm. of certified pure boric acid crystals in 1 liter of ammonia free distilled water (this may be accomplished by placing permutit in container of distilled water and shaking).

Sulfuric acid---0.05 N

Methyl red indicator.

Procedure: Titration should be undertaken with white porcelain plate to match colors. A blank should be run on the reagents used, the color of which should be matched.

Take flask into which distillate has been collected. Add 3 drops of methyl red indicator and titrate the ammonia with 0.05 N sulfuric acid, matching the end point with that of the blank containing the same reagents and distilled in a similar fashion as other samples.

8. Calculation of total base exchange capacity:

The cation exchange capacity of the sample at any particular pH value, in milli-equivalents per 100 gm. of dry soil may be expressed as:

$$B.\ E.\ C. = \frac{100\ N\ (B-T)}{W}$$

N   normality of titrating sulfuric acid
B-T ml. of titrating agent used to match color with that of blank
W   weight of dry sample in gms.

TABLE I

PREPARATION OF AMMONIUM ACETATE SOLUTIONS

For Desired pH Solution, Mix following Amounts of Reagents (in milliliters)

pH	Acetic Acid (17.6 N)	Acetic Acid (5 N)	Amm. Acetate (1 N, pH 7)	NH_4OH (1 N)	NH_4OH (15.1 N)
4	366.5	--	--	--	66.2
5	107.0	--	--	--	66.2
6	--	16.2	1000*	--	--
7	--	--	1000	--	--
8	--	--	980.	20	--
9	--	--	833.3	--	11.02
10	--	--	85.4	--	61.9
11	--	--	12.8	--	65.4

* Final Dilution to 1016.2 ml.
All other dilute to 1000 ml.

The above solutions were prepared and then checked periodically by a Beckman pH Meter.

Procedure for Determination of Organic Matter in Clay Samples

The procedures for the determination of total B. E. C. suggested by J. S. Hosking and used exclusively in our investigation differs for samples with or without organic matter. Since organic matter oxidizes in hydrogen peroxide, any loss in weight of the sample would indicate its presence. The following simple test was used to ascertain its presence or absence:

1. Weigh oven-dry sample (105 C)
2. Saturate with hydrogen peroxide (30% Cert. Pure)
3. Dry sample in oven at 105 C
4. Weigh sample. The loss in weight after treatment with hydrogen peroxide may be expressed as percentage by weight of organic matter.

C. Procedure for Spectrographic Analysis

Plate Calibration

As stated before the amount of each element present will determine the relative intensities of its spectral lines on the plate. In general the relationship between the amount present and the line intensity is expressed by the equation:

$\log C = K_1 \log I\,t + K_2$ (1)

C = concentration

I = line intensity

t = time of exposure

$K_1 . K_2$ are constants

By applying this relationship to two elements and subtracting we get

$$\log \frac{C_1}{C_2} = \log \frac{(I_1\,t)^{K_1}}{(I_2\,t)^{K_2}} + \text{constant} \qquad (2)$$

If element 2 is one whose concentration is known to remain constant, it is termed an internal standard and we may write $\log C = K_3 \log \frac{I_2}{I_1} + \text{constant}$ (3)

C = concentration

I = Relative intensity of analysis line

I = Relative intensity of internal standard line

K_3 is a constant

Consequently concentration can be determined from a graph on which concentration is plotted against intensity ratio or any function of intensity ratio.

In order to determine values of $\frac{I_2}{I_1}$ it is necessary to calibrate the emulsion so that density readings from

a densitometer may be converted to intensity readings.

One method which works very well is the "two line" method, so called, because two known spectral lines are used whose intensity ratio remains constant under ordinary operating conditions over a wide range of exposures. These lines should also lie within a suitable wave length range, be sharply defined and be free from interfering effects by other elements.

The lines used were the iron lines 3047.6 and 3037.4. A set of graded exposures from weak to strong were made by varying the degree of opening of the rotating sector. Densitometer deflections were measured and the preliminary curve drawn from the corresponding deflections.

Emulsion Calibration Curve

If the ratio of the two iron lines mentioned above is r, this preliminary curve can now be used for any given density to determine the density corresponding to a fractional intensity increase of r. This gives a means of plotting density against log of relative intensity, i. e. starting with a density value which represents, say, the lightest reading that will be required in analysis, a relative intensity of 1 will be chosen for this point. Then for an intensity of $r \times 1 = r$ the next density point will be read from the preliminary curve, and for the next intensity $r \times r = r^2$ the next density, etc. A table will therefore be built as follows:

Read. #	Density	Rel. Intensity	Log Rel. Int.
0	D_0	1	0
1	D_1	r	log r
2	D_2	r^2	2 log r
3	D_3	r^3	3 log r

Since log r is a constant we now note that we are plotting our density values against a successively repeating constant interval, and that any convenient constant can be used for r since in analysis we calculate relative intensities.

Working Curves

It has been previously shown regarding the concentration of an element that:

$$\log C = K_1 \log \frac{(I_a)}{(I_s)} + \text{constant} \qquad (3)$$

I_s is the intensity of a line of the so-called "internal standard" which is in general a line of the matrix constituent or a constituent known to be present in approximately constant percentage in both standards and samples. It is seen that a plot of concentration v.s. $\frac{I_a}{I_s}$ (or a constant function of that ratio) on log-log paper should be a straight line and that it will be a simple matter using the densitometer readings and emulsion calibration curve to evaluate $\frac{I_a}{I_s}$ for any known system. Once such a plot is established it can be used to determine composition for unknown material when the value of $\frac{I_a}{I_s}$ has been obtained. Since these curves are then the basis for analysis, they have been termed "working curves."

Due to the many variables involved in the preparation of the spectrum, the working curves have been found to shift from day to day in spite of rigorous control of the processes. In general, however, the constant K is not affected by such fluctuations so that the shifted curve is generally parallel to the original. Corrections may therefore be made by including one or two standard samples with every analysis to determine the magnitude of the shift.

Preparation of Samples for the Spectrograph

The samples were all prepared using the same method as Reuss employed in his investigation. One part sample is mixed with five parts sodium fluoride and twelve parts graphite.

Two factors affect the methods of preparation used. First, the method of preparation should not be time consuming, and secondly, the preparation should be carried out with the aim of reducing the mineralogical differences of the clay standards and unknowns.

Reuss found that for runs on plain samples there was a definite lack of analysis lines, and low density for those present because of the high non-conducting nature of the clay minerals. The addition of graphite resulte d in too great intensities at 2 KVA power; and at 2/3 KVA power, the mineralogical differences produced discrepancies. To eliminate this latter error, a flux of sodium flouride was added. The power used was 2 KVA which increased the flux action during the longer prespark time. The net result was a sample whose crystal structure was destroyed before the exposure was made, and a decrease in mineralogical differences.

In making a run for quantitative analysis and determination of adsorbed ion content, it is necessary to include on the same plate spectra of the following: iron for locating position on the plate, two or three

clay standards to check working curves, and two or three samples of both treated and untreated unknown clays.

PART V

RESULTS

A. Base Exchange Capacity Determinations

B. Spectrographic Analysis

RESULTS

Results of BEC Determinations

A. Max. BEC for the three clay types investigated occurs approximately at pH 9.

B. Max. BEC of KAOLINITE averaged 7.9 me/100 gm. (Fig. D)
Max. BEC of ILLITE averaged 17.5 me/100 gm. (Fig. E)
Max. BEC of MONTMORILLONITE averaged 79.0 me/100 gm. (Fig. F)

C. Comparison of results of BEC on mixed sample and arithmetic proportions of results of the components given above:

Arithmetical: (BEC taken from results on graphs)

Clay Type	Max. BEC	BEC/3	pH
KAOLIN	7.9	2.6	8.9
ILLITE	17.5	5.8	8.7
MONTMOR-ILLONITE	79.0	26.0	9.0
		Σ = 34.4 me/100 gm.	

BEC of mixed sample at pH 9 = 26.5 me/100 gm. (Mean value indicated on graph Fig. G)

D. None of the clay minerals tested exhibited the presence of any appreciable amount of organic matter (Table II).

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

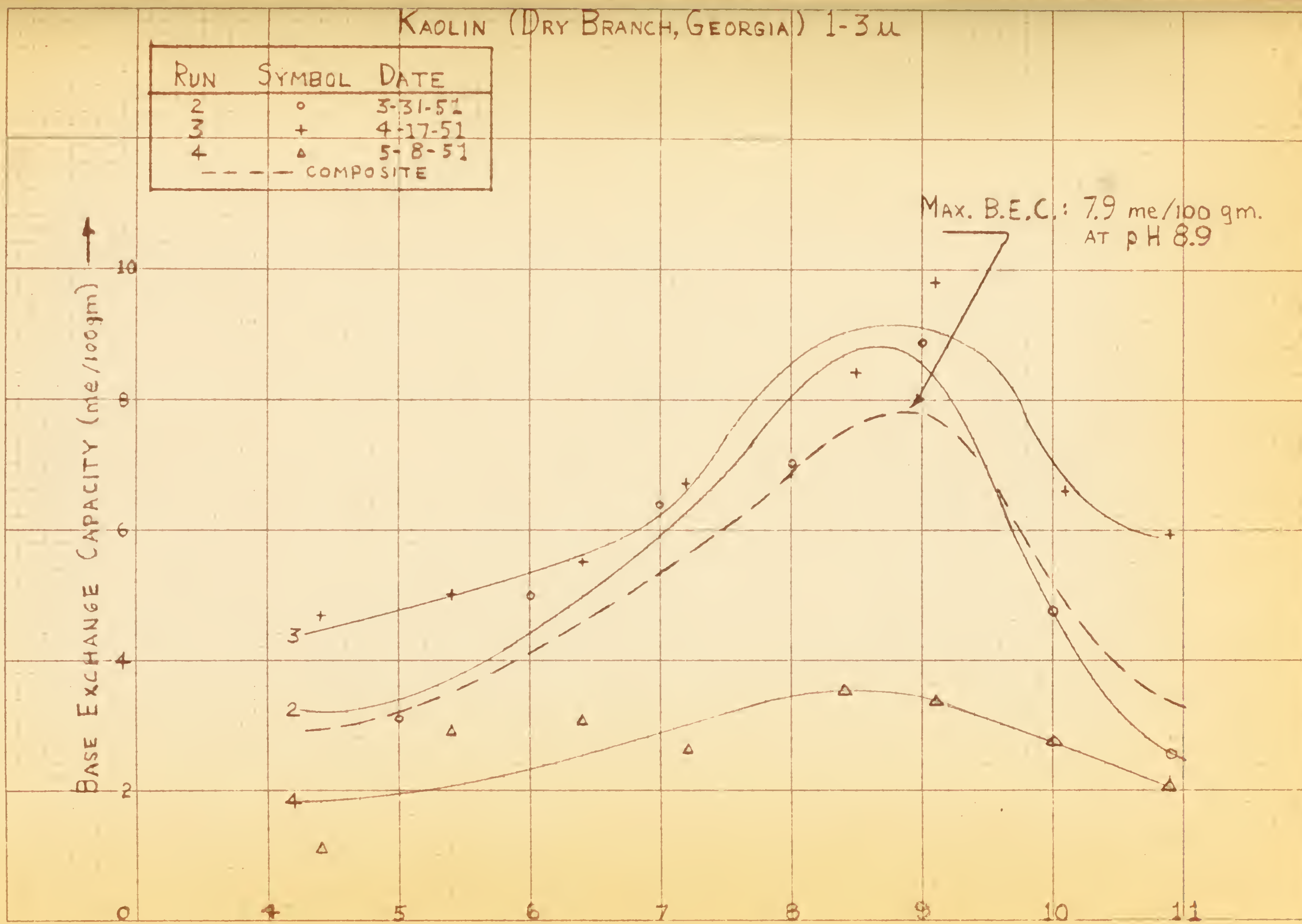
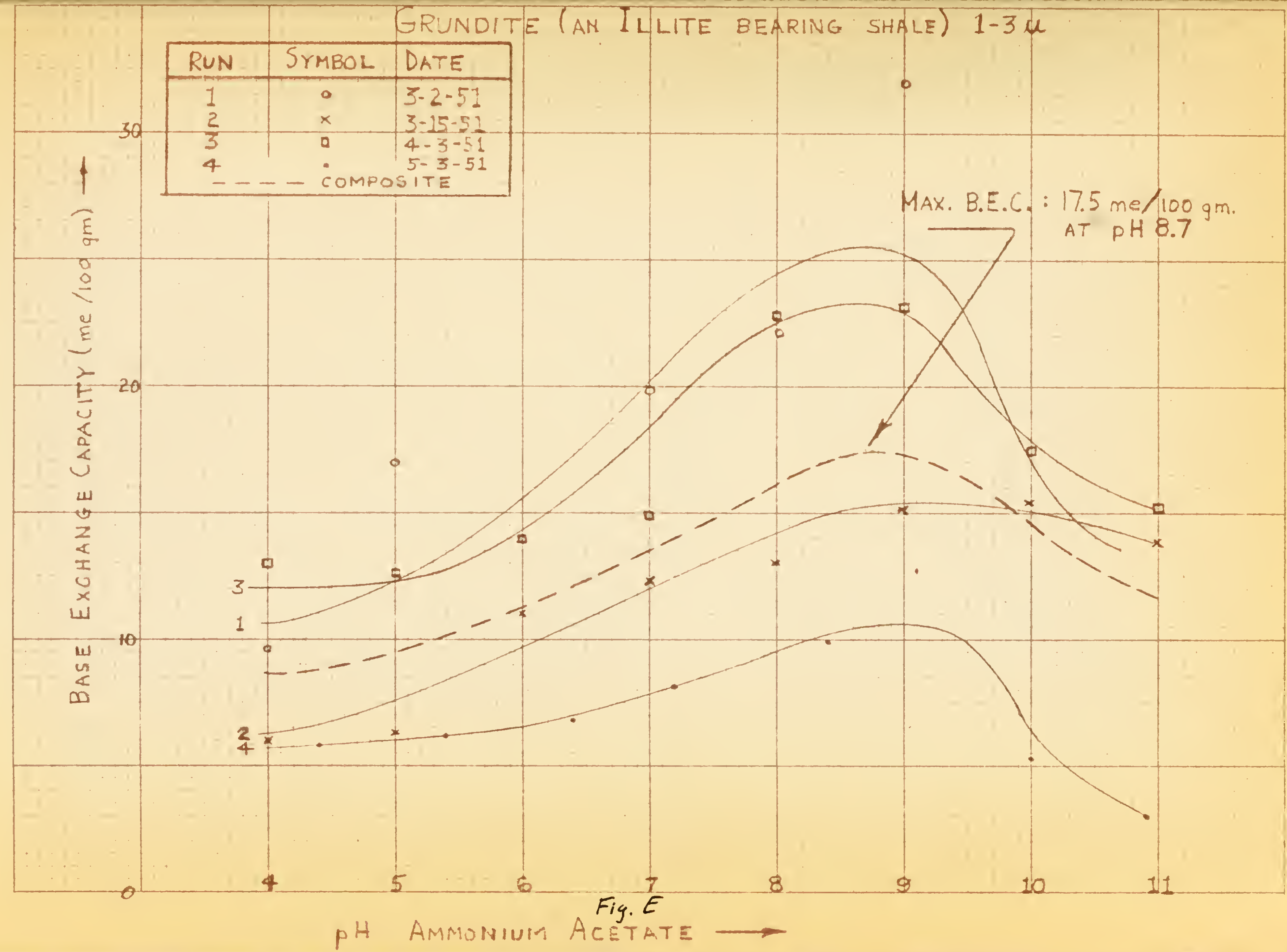
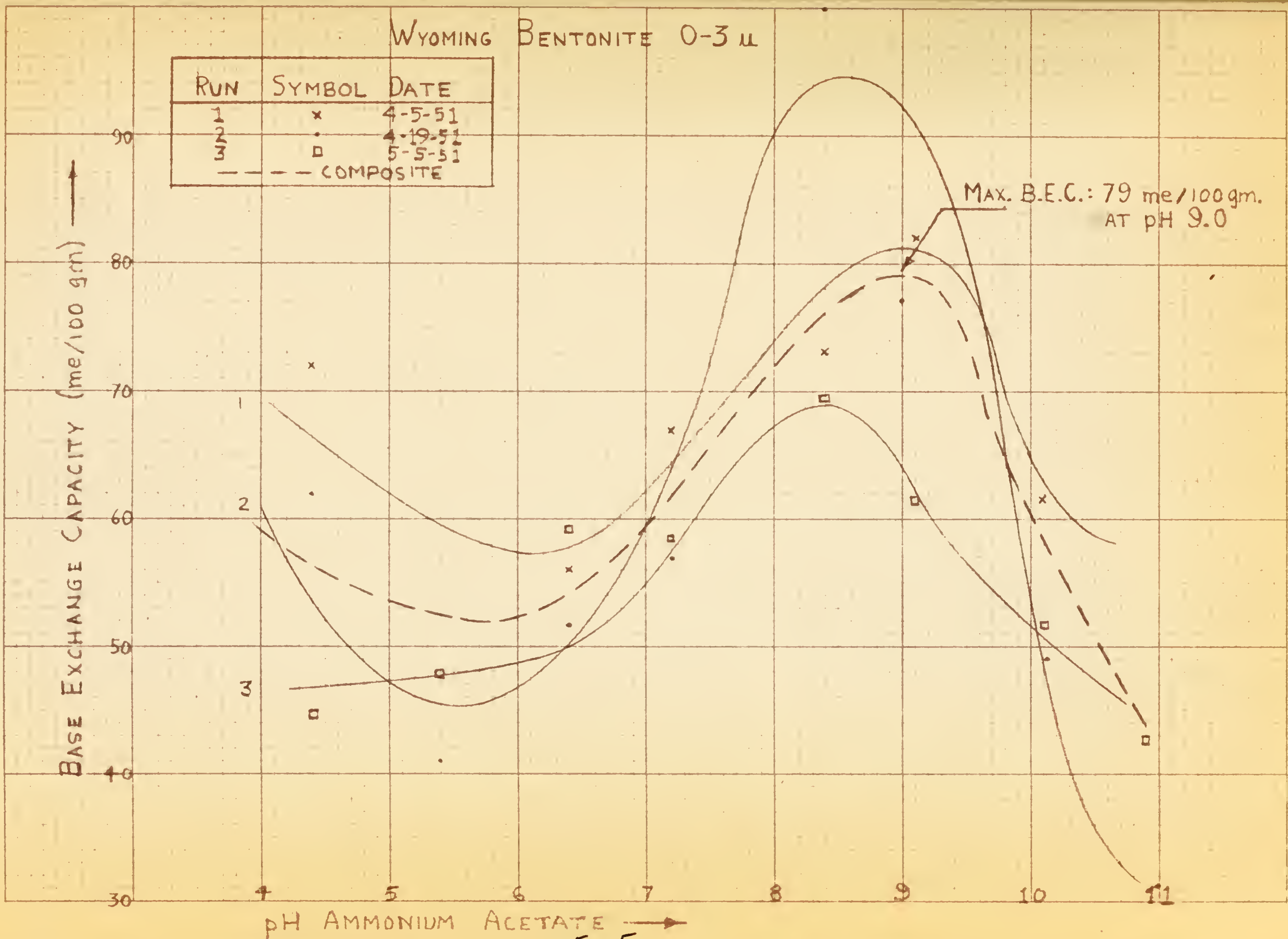

KAOLIN (DRY BRANCH, GEORGIA) 1-3 μ
RUN SYMBOL DATE
2 o 3-31-51
3 + 4-17-51
4 Δ 5-8-51
COMPOSITE
MAX. B.E.C.: 7.9 me/100 gm.
AT pH 8.9
BASE EXCHANGE CAPACITY (me/100gm)
pH AMMONIUM ACETATE
0
2
4
6
8
10
4
5
6
7
8
9
10
11

Fig. D



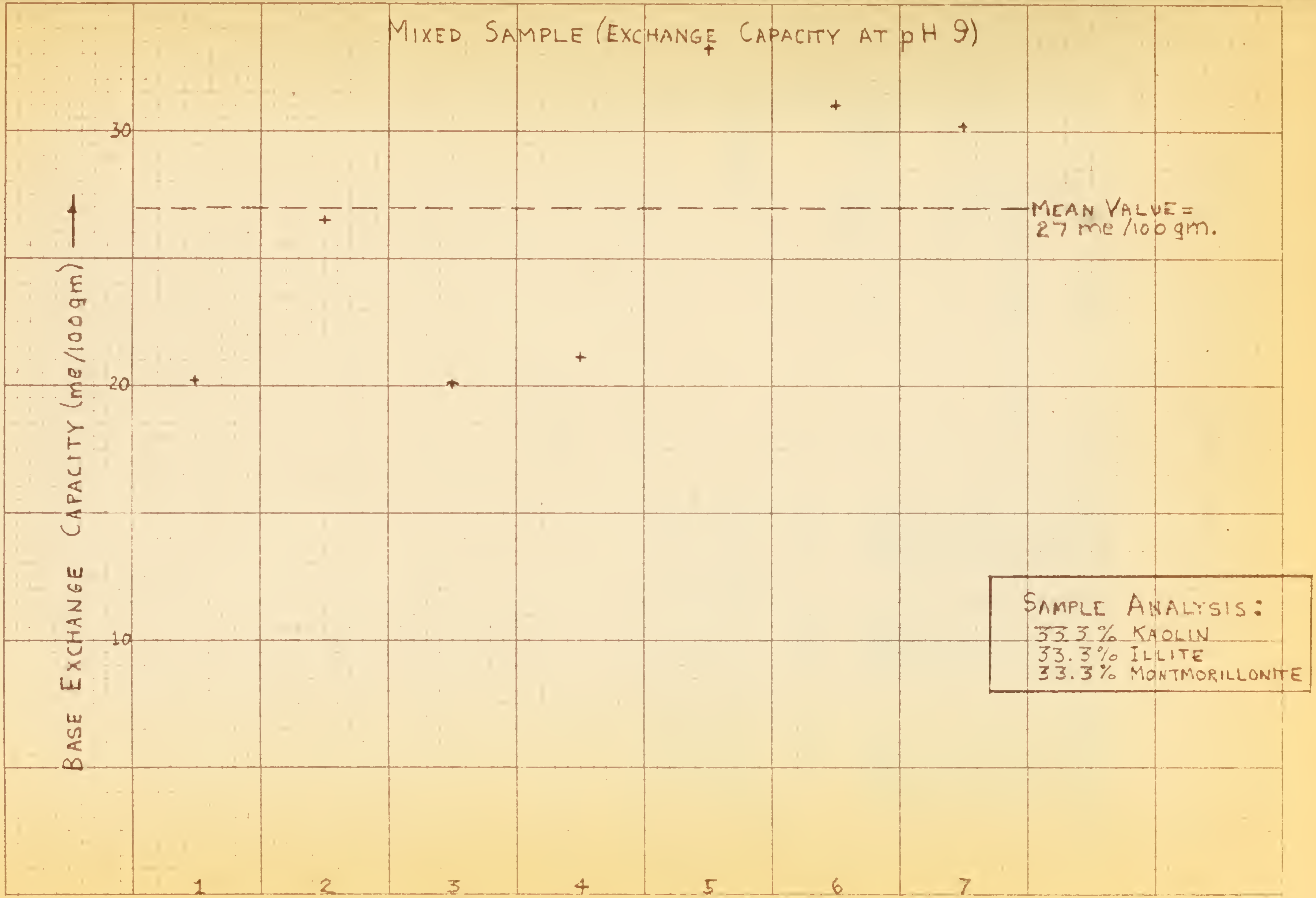
GRUNDITE (AN ILLITE BEARING SHALE) 1-3 μ
RUN SYMBOL DATE
1 o 3-2-51
2 x 3-15-51
3 □ 4-3-51
4 • 5-3-51
- - - - COMPOSITE
MAX. B.E.C. : 17.5 me/100 gm. AT pH 8.7
BASE EXCHANGE CAPACITY (me/100 gm)
0
10
20
30
4
5
6
7
8
9
10
11
3
1
2
4
pH AMMONIUM ACETATE

Fig. E



WYOMING BENTONITE 0-3 µ
RUN SYMBOL DATE
1 × 4-5-51
2 • 4-19-51
3 □ 5-5-51
COMPOSITE
MAX. B.E.C.: 79 me/100 gm. AT pH 9.0
BASE EXCHANGE CAPACITY (me/100 gm)
pH AMMONIUM ACETATE
1
2
3
90
80
70
60
50
40
30
4
5
6
7
8
9
10
11

Fig. F



MIXED SAMPLE (EXCHANGE CAPACITY AT pH 9)
MEAN VALUE = 27 me/100 gm.
SAMPLE ANALYSIS:
33.3% KAOLIN
33.3% ILLITE
33.3% MONTMORILLONITE
BASE EXCHANGE CAPACITY (me/100gm)
30
20
10
1
2
3
4
5
6
7
NUMBER OF TEST

Fig. G

RESULTS OF ORGANIC MATTER DETERMINATIONS

	KAOLIN	ILLITE	BENTONITE
Wt. Sample + Dish Wt. Dish Wt. Sample	21.9557 17.4678 4.4879gm	95.5792 87.1362 8.4430	21.0014 17.0057 3.9957gm.
Wt. treated Sample + Dish Wt. Dish Wt. Sample	21.9496 17.4678 4.4818gm	95.5785 87.1362 8.4423	20.9735 17.0057 3.9678gm.
Loss in Wt.	4.4879 4.4818 0.0061gm	8.4430 8.4423 0.0007	3.9957 3.9678 0.0279gm.
% Organic = $\frac{\text{Loss in wt.}}{\text{Wt. Sample}}$ x 100	$\frac{0.0061}{4.4818}$ 100 = 0.14%	$\frac{0.0007}{8.4423}$ 100 = 0.01%	$\frac{0.0279}{3.9678}$ 100 = 0.7%
COMMENT:	Inappreciable organic material present in all types. Therefore, same procedure may be used for exchange capacity determinations.		

TABLE II

RESULTS

Results of Spectrograph Analysis

The preliminary curve coincided with the curve used by Reuss and also with the curve in use in the Metallurgy Department. Therefore, it was unnecessary to solve for the emulsion calibration curve which is the same as Reuss's and the one in use in the Metallurgy Dept. (Fig. H,I)

The analysis of the standards used plotted on a straight line parallel to the original working curves of Reuss. Therefore, it was assumed that the working curves merely shifted parallel to themselves as explained in the procedure. (Fig. J)

The results of the quantitative and qualitative analysis of the untreated and the treated (H-Clays supplied by Ennis and Hufft and prepared in conjunction with their thesis "An Investigation of the Effect of Ionic Substitution on the Atterberg Plasticity Constants of Certain Clay Minerals") clay samples are listed in Table III.

By converting the difference in per cent of the metallic oxides considered exchangeable present in the treated and untreated samples to milliequivalents per 100 grams of sample, the partial and total base exchange was calculated (Table IV). The total base exchange values thus computed were as follows:

KAOLINITE 6.92 me/100 gm., Illite 25.1 me/100 gm. and BENTONITE 50.29 me/100 gm.

PRELIMINARY CURVE

Settings

Power	2/3 KVA
Inductance	8 millihenries
Slit Width	50 microns
Wave length range	2400-3800 A°
Prespark	5 seconds
Exposure	17 seconds
Electrodes	Iron
Plates	Eastman Kodak No. 1 Spectrum Analysis

Line	Rack	Sector	Densitometer λ 3037A°	Deflections 3047A°
1	350	70°	.149	.161
2	375	45°	.072	.083
3	400	22°	0	0
4	425	11°	0	0
5	450	90°	.218	.235
6	475	120°	.312	.330
7	500	180°	.615	.640
8	525	Open	1.140	1.17

PRELIMINARY CURVE (FROM REUSS)

DENSITOMETER DEFLECTIONS

IRON SPECTRUM
LINE 3047 vs 3037

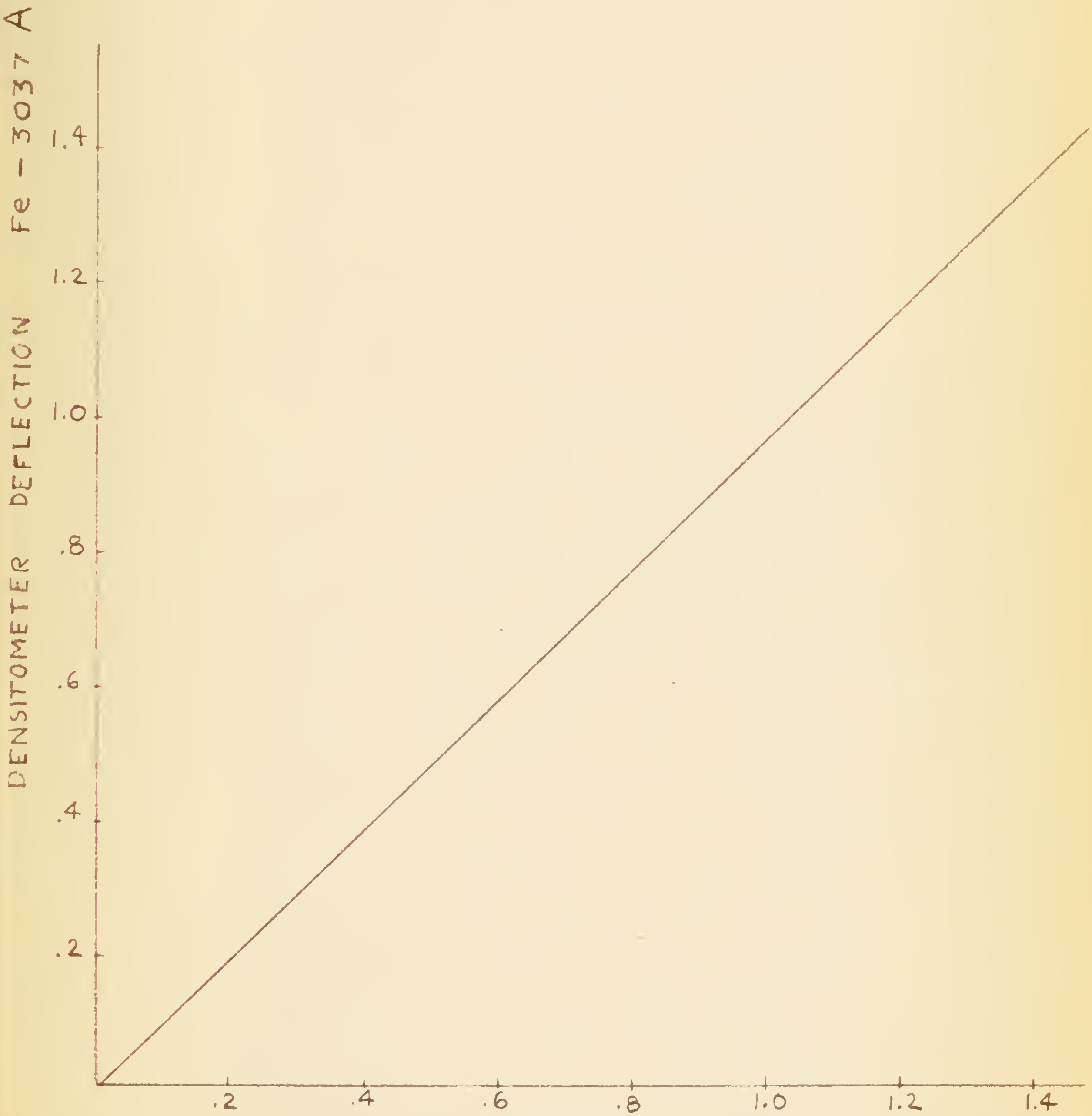


FIG - H

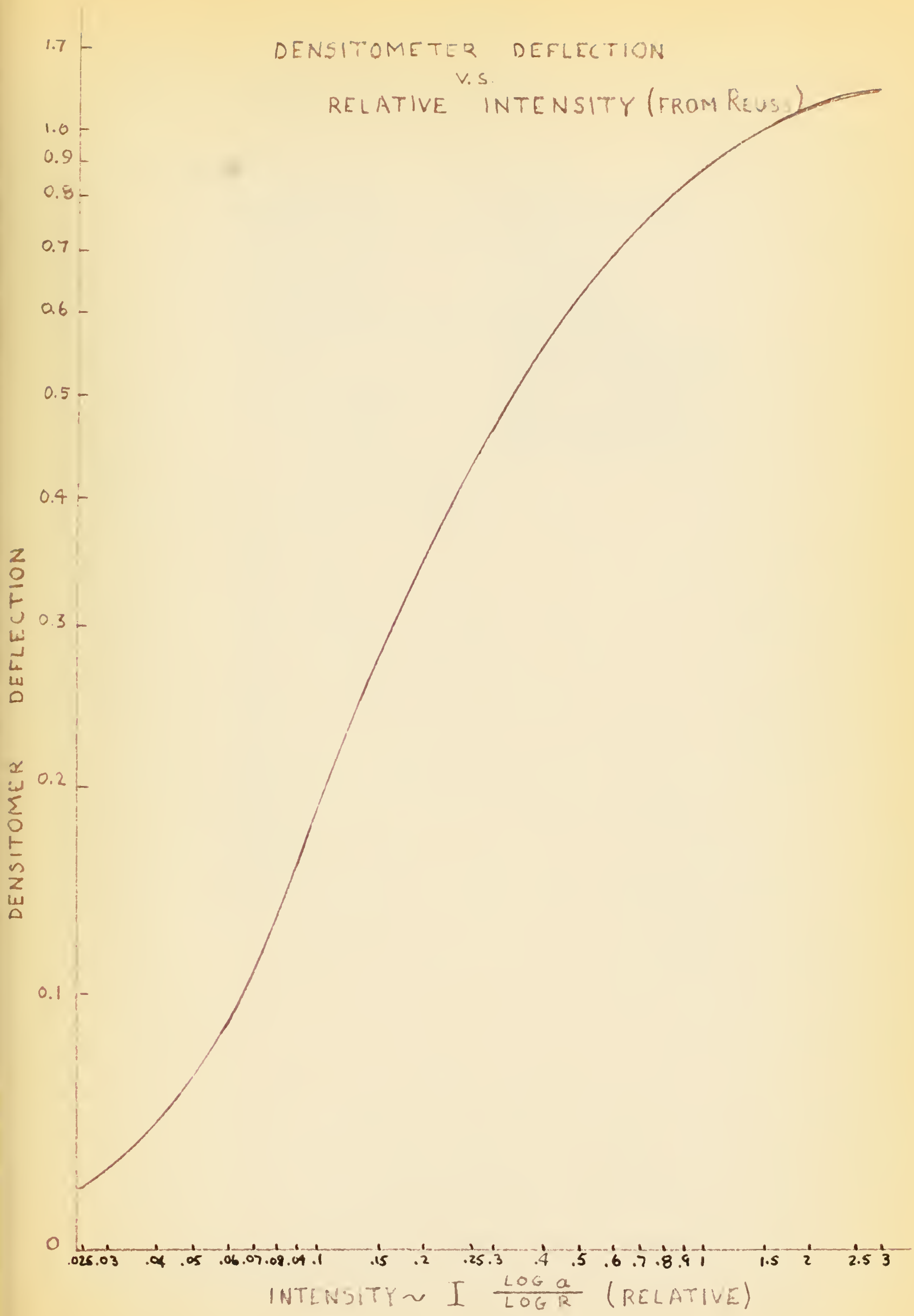

DENSITOMETER DEFLECTION
V.S.
RELATIVE INTENSITY (FROM REUSS)
DENSITOMER DEFLECTION
1.7
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
.025 .03 .04 .05 .06 .07 .08 .09 .1 .15 .2 .25 .3 .4 .5 .6 .7 .8 .9 1 1.5 2 2.5 3
INTENSITY ~ I LOG a / LOG R (RELATIVE)

FIG.-I

ANALYSIS

Sample: 1 Part Standard Clay
5 Parts Sodium Fluoride
12 Parts Graphite

Settings:

Power	2 KVA
Inductance	8 millihenries
Slit Width	50 microns
Gap	3 m.m.
Prespark	5 seconds
Exposure	20 seconds
Wavelength Range	2400-3800 A°
Plate	Eastman Kodak #1 Spectrum Analysis
Development	6 min. 18.5°C D-19 Solution
Electrodes	High Purity Carbon

Lines used in the Analysis

Si	2988
Fe	2599
Al	3066
Ca	3006
Ti	3261
Mg	3332
K	3217
Na	3189

Sample IRON	Line	Rack	Remarks
	1	450	Full Sector
	2	475	90° Sector
B-stand.	3	500	
K-stand.	4	525	
I-stand.	5	550	
B	6	575	
K	7	600	
I	8	625	
H-B	9	650	
H-K	10	675	
H-I	11	700	

STANDARD BENTONITE

	Wave Length	Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.
Si	2988	.276	.176		
Fe	2599	.299	.193	1.10	.0487
Al	3066	.353	.238	1.35	.30
Mg	2795	.571	.545	3.09	.0485
Ca	3006	.072	.055	.31	.00164
Na	3189	.770	1.09	6.20	.0236
K	3217	.033	.037	.21	.00508
Ti	3261	.010	.004	.02	.00131

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

STANDARD KAOLINITE

	Wave length	Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.
Si	2988	.262	.164		
Fe	2599	.060	.049	.30	.0107
Al	3066	.830	1.23	7.5	.7730
Ca	3006	.301	.205	1.25	.0130
Ti	3261	.860	1.475	9.0	.0282
Mg	3332	.012	.0155	.095	.0056
K	3217	.060	.049	.30	.0096
Na	3189	.550	.492	3.0	.0089

STANDARD ILLITE

Wave Length		Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.
Si	2988	.108	.076	. .	
Fe	2599	.200	.125	1.65	.0915
Al	3066	.159	.103	1.36	.3130
Ca	3006	.113	.085	1.12	.0112
Ti	3261	.449	.342	4.50	.0143
Mg	3332	.225	.145	1.90	.0392
K	3217	.018	.023	.30	.1002
Na	3189	.112	.084	1.10	.0026

WORKING CURVES (FROM REUSS)

DENSITY RATIO VS CONCENTRATION RATIO

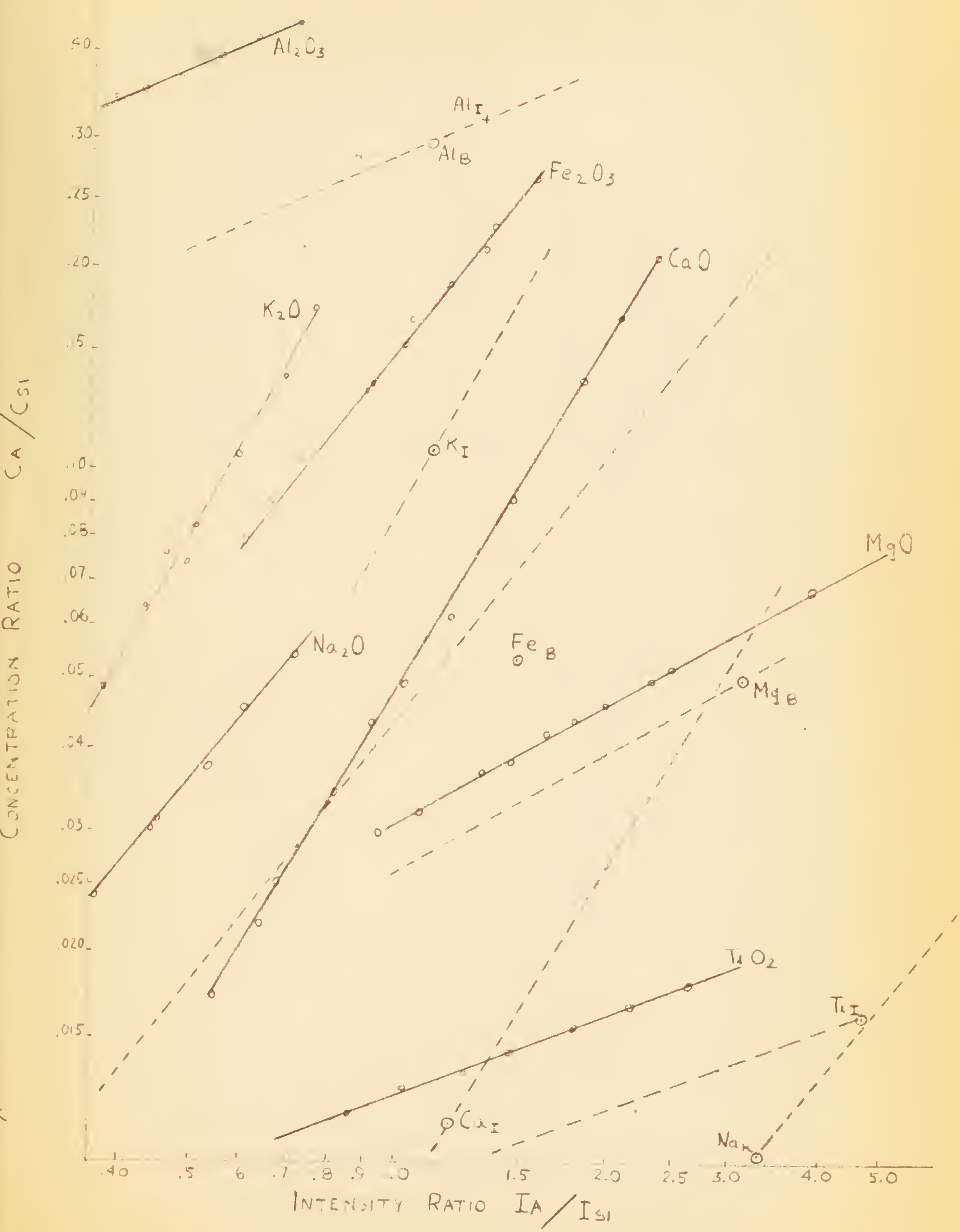


FIG-J

UNTREATED BENTONITE

Wave Length		Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.	% Oxide
Si	2988	.725	1.05			81.3
Fe	2599	.571	.63	.60	.0253	2.06
Al	3066	.023	.027	.026	.0565	4.60
Ca	3006	.405	.304	.29	.00115	.094
Ti	3261	.062	.053	.05	.0025	.203
Mg	3332	1.01	2.00	1.90	.0374	3.04
K	3217	.310	.22	.21	.00394	0.32
Na	3189	1.05	2.52	2.4	.00616	.50

UNTREATED ILLITE

Wave Length		Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.	% Oxide
Si	2988	.562	.55			52.0
Fe	2599	.871	1.56	2.85	.166	8.60
Al	3066	.708	.96	1.75	.383	19.90
Ca	3006	.478	.396	.72	.0047	.243
Ti	3261	1.40	4.40	8.0	.0203	1.055
Mg	3332	.478	.396	.72	.0223	1.16
K	3217	.582	.66	1.20	.132	6.85
Na	3189	.610	.715	1.30	.0025	.132

UNTREATED KAOLINITE

	Wave Length	Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.	% Oxide
Si	2988	.106	.072			50.2
Fe	2599	.072	.055	.76	.0351	1.76
Al	3066	.510	.424	5.9	.596	29.9
Ca	3006	.020	.028	.39	.00205	.103
Ti	3261	.740	1.08	15	.0295	1.48
Mg	3332	.160	.104	1.45	.0301	1.51
K	3217	.053	.045	.63	.0411	2.06
Na	3189	.450	.36	5.0	.0175	.875

TREATED H-BENTONITE

Wave Length		Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.	% Oxide
Si	2988	.78	1.10			81.00
Fe	2599	.61	.65	.59	.02470	2.00
Al	3066	.019	.027	.025	.05500	4.450
Ca	3006	.014	.011	.01	.00005	.004
Ti	3261	.014	.011	.01	.00127	.103
Mg	3332	.84	1.32	1.20	.02810	2.280
K	3217	.30	.198	.18	.00346	0.280
Na	3189	.97	2.20	2.0	.00494	.400

TREATED H-KAOLINITE

Wave Length		Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.	% Oxide
Si	2988	.318	.208			49.9
Fe	2599	.262	.162	.78	.0353	1.76
Al	3066	.81	1.25	6.0	.602	30.1
Ca	3006					0
Ti	3261	1.10	3.12	15	.0295	1.47
Mg	3332	.339	.302	1.45	.0301	1.50
K	3217	.195	.123	.59	.0401	2.00
Na	3189	.73	1.0	4.8	.0170	.845

TREATED H-ILLITE

Wave Length		Dens. Deflec.	Emuls. Cal.	Intens. Rat.	Conc. Rat.	% Oxide
Si	2988	.577	.63			52.6
Fe	2599	.842	1.57	2.50	.140	7.36
Al	3066	.730	1.13	1.8	.390	20.6
Ca	3006	.536	.505	.80	.0006	.030
Ti	3261	1.15	3.34	5.3	.0177	0.93
Mg	3332	.443	3.85	.61	.0196	1.03
K	3217	.633	.725	1.15	.127	6.66
Na	3189	.644	.79	1.25	.00211	.111

TABLE III

SAMPLE	% SiO_2	% Al_2O_3	% Fe_2O_3	% CaO	% TiO_2	% MgO	% K_2O	% Na_2O	Ignition Loss %	Total %
Kaolinite (Untreated	50.2	29.9	1.76	.103	1.48	1.51	2.06	.875	12.24	100.128
Hydrogen-Kaolinite	49.9	30.1	1.76	0	1.47	1.50	2.00	.845	12.83	100.405
Illite (Untreated)	52.0	19.9	8.60	.243	1.055	1.16	6.85	.132	9.84	99.780
Hydrogen Illite	52.6	20.6	7.36	.030	0.93	1.03	6.66	.111	10.03	99.351
Bentonite (Untreated)	81.3	4.60	2.06	.094	.203	3.04	0.32	.500	7.85	99.967
Hydrogen Bentonite	81.0	4.45	2.00	.004	.103	2.28	0.28	.400	9.34	99.857

TABLE IV

SAMPLE	B.E.Value (Spectrograph)	Av. Max.BEC (Amm.Dist.)	Max. BEC* (Potentiometric Titration)
KAOLINITE	6.92	7.9	2.27
ILLITE	25.1	17.5	10
BENTONITE	50.29	79.0	35

NOTE: All values in me/100 g

*As determined by Ennis and Hufft.

VI

Conclusions and Recommendations

A. Preparation of Samples for B. E. C. Determinations.

B. Base Exchange Capacity

C. Spectrographic Analysis

Conclusions and Recommendations

A. Preparation of Sample

As stated in the procedure a different method of particle separation was employed for each of the three clay types investigated. The relative merit of each method will now be discussed.

Gravitational Separation

Gravitational sedimentation was the easiest method. It involved no attention during the settling period, requiring only dispersion with the high-speed mixer at the outset and decantation after the calculated time interval. The desired fraction however, was in a saturated state and necessitated drying for weight measurements.

Separation by Centrifugation

Centrifugation was a more expeditious method of separation, but required more attention of the operator. The resultant fraction was saturated.

Separation by Roller Analyzer

Separation by this method required many more man-hours of operation and was more tedious than either of the other methods. Twenty-five hours of full-time operation yielded only five grams of Wyoming Bentonite.

Advantages and Disadvantages

The primary advantage of sedimentation and centrifugation is the comparative ease with which the sample is obtained. However, both methods furnish a saturated sample. Subsequent drying for the necessary weight measurements results in an unmeasurable degree of reaggregation. The desired particle size has been

enlarged an unknown amount.

On the other hand the sample produced by the Roller Analyzer is more nearly the desired size. Operation of this apparatus is more tedious than either of the fore-mentioned methods.

Selection of method will therefore be dependent on whichever consideration is of paramount importance; ease of separation, or accuracy of the particle size separated.

B. Base Exchange Capacity Determinations

There are two major reasons why determination of exchange capacity by the ammonia distillation method is simpler than other methods; 1) the ease of disassociation of ammonia from the clay upon heating and the simple titration associated with its release and 2) the need for only small amounts of test sample. Since considerable time must be spent to separate clay samples in the colloidal range, any method requiring small quantities of sample is preferable. It is a relatively rapid method for measuring the change in B. E. C. with varying pH.

It was found that the B. E. C. varies over the range of pH, reaching a maximum at pH 9 for all three clay types. Noticeable discrepancies for maximum B. E. C. are noted for each parameter, however the rate of change of exchange capacity with pH is quite similar. This bears out the importance of proper laboratory technique in the distillation procedure. Reagents must be accurately prepared and kept up to strength, and the distillation procedure must be meticulously followed. The average or composite curves are in agreement with Hosking's report and extends his findings to include Illite.

A series of tests of a laboratory mixture of equal parts of the three clay minerals indicated a total B. E. C. approximately proportional to the per cent by weight of the exchange capacities of the component parts.

The following recommendations seem justified after concluding our tests. Modification of the Procedure suggested by J. Munzer where boric acid is substituted for standard hydrochloric acid

[illegible]

proved to be a judicious one. It has been found in sewage analysis that distillation into boric acid was easier, more accurate, and furnished closer duplication of results than distillation into hydrochloric acid. Insertion of two glass beads in each distilling flask counteracts the tendency to superheat and reduces the consequent "bumping" (vigorous boiling). Another change in Hosking's procedure concerned the use of a color indicator in the titration process. Methyl red was found to be the best indicator, and we suggest the use of seven drops of indicator for facility in matching colors in the titration process. The phrase "base exchange capacity" is insufficient. Since the exchange capacity of a soil varies both by the specific method utilized and the pH it can be stated correctly only by reference to those variables. We suggest the complete phrase be "the maximum base exchange capacity as determined by the process of ammonia distillation at pH 9 is ----." This connotation conforms to repeated experimental results that the B. E. C. is a maximum at pH 9.

If more time was available, it would be interesting to compare the results obtained by this method with those secured from a thorough chemical analysis of the constituents.

C. SPECTROGRAPHIC ANALYSIS

The preparation of samples and general procedure as developed by Reuss proved highly satisfactory. The use of high purity carbon electrodes and graphite serves to lower the amount of impurities. However, there are certain serious limitations that very definitely affect the results of an analysis. First, the accuracy of the percentage of any one element present depends on the accuracy of the analysis for all the other elements present; second, the effect of mineralogical differences in all types of clays may not be completely removed by the addition of sodium fluoride; third, the addition of the sodium fluoride itself will introduce impurities into the sample; fourth, the range covered by the working curves is small; and fifth, the limitation imposed by the resolving power of the spectrograph itself such that all elements are not discernible in the spectrum (e.g. Hydrogen and Lithium).

It is of interest to note that the emulsion calibration curve coincided with that of Reuss, drawn two years ago (1949). This speaks well for Eastman Kodak's emulsifying process.

The drift of the working curves must be checked every time a run is made on an unknown. This is easily done by including a known standard on each plate.

Before any accurate conclusions may be drawn con-

cerning the accuracy of the quantitative and qualitative analysis of the unknown clays as well as their adsorbed ion content, it would be preferable to analyze other samples chemically. However, because of the time required for such an analysis and the degree of accuracy required, it is felt that the spectrograph provides a relatively simple means of analysis and will fall within the range of accuracy required.

The clay samples prepared by Ennis and Hufft were treated with hydrochloric acid to form H-clays. It is felt that for better correlation of the base exchange as measured by spectrographic analysis with the base exchange capacity as found by the chemical method developed by Hosking$_7$, an ammonium saturated clay (saturated in the same manner as for determination of BEC) should be used. The results of this phase of the investigation, therefore, merely measure the amount of hydrogen ions adsorbed by each clay in displacing previously attached ions. Thus, this base exchange value only measures a certain degree of the total base exchange capacity depending on the extent and time of treatment of the samples.

In comparing these base exchange values with the average maximum base exchange capacities as previously determined, it is seen that for Kaolinite, approximately 88% of exchange has taken place and for Bentonite, approximately 64%. For Illite, the average value of base ex-

change capacity is only 17.5 me/100g, which is less than the exchange value 25.1 me/100g. Referring to Fig. E, however, it is noted that Illite in two runs had a maximum base exchange capacity of 23.1 me/100g which decreases the apparent error. The marked variation in values of maximum base exchange capacities for the Illite would seem to substantiate the base exchange value 25.1 me/100g and that may very well be the true maximum base exchange capacity for the Illite.

It must be remembered that other cations may be present on the samples analyzed. In our work we studied the cations which we considered of major importance, not subject to limitations imposed by the resolving power of the spectrograph, and most likely to occur in measurable quantities. It is felt that any other cations that might actually be adsorbed in the clays studied, would appear in such small quantities as not to affect the results.

Time did not permit further spectrographic analysis of various homoionic clays. Future work should very definitely be done along these lines with emphasis on correlation with x-ray diffraction and base exchange capacity. If possible, it would be advisable to run a chemical analysis also, so that more positive conclusions can be drawn.

However, it is felt that spectrographic analysis can be used for calculating degrees of base exchange and also

for maximum base exchange capacities for clays where complete replacement by hydrogen or ammonium ions has occurred. It is hoped that techniques used in this investigation will prove of service to future investigators.

PART VII

APPENDIX

A. Data

(1) BEC Tests

(2) Spectrographic Analysis

B. Sample Computations

C. References

KAOLINITE RUN #1
March 21, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05N H_2SO_4 used for Titration (mls.)	Base Exchange Capacity = 100 N (B-T) ÷ W
0.1086	4	1.31 0.01 1.3	$\frac{100(.05)1.3}{0.1086} = 59.9$
0.1133	5	2.59 1.32 1.27	$\frac{100(.05)(1.27)}{0.1133} = 55.9$
0.1055	6	4.99 2.60 2.39	$\frac{100(.05)(2.39)}{.1055} = 113.2$
0.0730	7	1.11 0.01 1.10	$\frac{100(.05)(1.10)}{.0730} = 75.3$
0.0806	8	1.68 1.14 .54	$\frac{100(.05)(.54)}{.0806} = 33.4$
0.1009	9	2.08 1.70 .38	$\frac{100(.05)(.38)}{.1009} = 18.8$
0.1225	10	2.90 2.09 .81	$\frac{100(.05)(.81)}{.1225} = 33.0$
0.1305	11		(Supernatant Liquid not clear)

COMMENTS: (1) Boric acid solution was made weaker by mistake, consequently, excessive H_2SO_4 was needed for back titration.

(2) Large pipette was used for titrating. It was difficult to match the color of sample with the blank.

(3) These results were considered invalidated for the above reasons, and were not included in graph.

[illegible]

KAOLINITE RUN #2
March 31, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05N H_2SO_4 used for Titration(mls.)	Base Exchange Capacity = 100 N (B-T) ÷ W
0.1090	4	0.59 0.42 0.07	$\frac{5(.07)}{0.1090} = 3.2$
.0965	5	2.38 2.32 0.06	$\frac{5(0.06)}{.0965} = 3.11$
0.1185	6	0.71 0.59 0.12	$\frac{5(.12)}{.1185} = 5.05$
0.0990	7	0.89 0.76 0.130	$\frac{5(.130)}{.0990} = 6.6$
0.1285	8	0.88 0.71 0.17	$\frac{5(.17)}{.1285} = 6.7$
0.1112	9	1.20 1.00 0.20	$\frac{5(.20)}{.1112} = 8.9$
0.1070	10	1.47 1.37 0.10	$\frac{5(.10)}{0.1070} = 4.7$
0.1033	11	2.43 2.48 0.05	$\frac{5(.05)}{0.1033} = 2.42$

COMMENTS: (1) Good control throughout

(2) Seven drops of methyl red indicator were used instead of three drops as stated in procedure. This modification resulted in easier matching of the colors for titration.

[illegible]

KAOLINITE RUN #3
April 17, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05N H_2SO_4 used for Titration (mls.)	Base Exchange Capacity = 100 N (B-T) ÷ W
0.0908	4	0.315 0.230 0.085	$\frac{5(.85)}{.0908} = 4.7$
0.1070	5	0.415 0.315 0.100	$\frac{5(.110)}{.1070} = 5.2$
0.1206	6	1.160 1.025 0.135	$\frac{5(.135)}{0.1206} = 5.6$
0.1043	7	0.640 0.480 0.160	$\frac{5(.160)}{.1043} = 7.6$
0.1134	8	1.340 1.160 1.180	$\frac{5\ (.180)}{.1134} = 7.9$
0.1057	9	0.885 0.675 0.210	$\frac{5(.210)}{.1051} = 9.9$
0.1315	10	1.735 1.580 0.175	$\frac{5(.175)}{.01315} = 6.65$
0.0927	11	1.580 1.470 0.110	$\frac{5(.110)}{.0927} = 5.9$

COMMENTS: (1) Samples underwent extended soaking period in ammonium aolution (84 Hrs.). This may account for higher values of exchange capacity.

(2) Denatured alcohol was used to wash away unattached ammonia.

KAOLINITE RUN #4
May 8, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration (mls.)	Base Exchange Capacity = 100 N(B-T) ÷ W
.0985	4	0.570 0.550 0.02	$\frac{5(.02)}{.0985} = 1.02$
.0717	5	0.628 0.585 0.043	$\frac{5(.043)}{.0717} = 3.0$
.0866	6	0.690 0.635 .055	$\frac{5(.055)}{.0866} = 0.32$
.1418	7	0.765 0.690 .075	$\frac{5(.075)}{.1418} = 2.65$
.1028	8	0.840 0.765 0.075	$\frac{5(.075)}{.1028} = 3.65$
.0835	9	1.320 0.840 .580	$\frac{5(.580)}{.0835} = 3.50$
.1046	10	1.374 1.320 .054	$\frac{5(.054)}{.1046} = 2.6$
.1043	11	1.421 1.375 .046	$\frac{5(.046)}{.1043} = 2.2$

COMMENTS: Good control

ILLITE RUN #1
March 2, 1951 (No organic matter)

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration (mls.)	Base Exchange Capacity = 100 N (B-T) ÷ W
0.0702	4	22.75 22.60 0.15	$\frac{100(.05)(.15)}{0.0762} = 9.85$
0.2364	5	6.0 5.2 0.8	$\frac{100(.05)(0.8)}{.2364} = 17.0$
0.0669	6	same color as blank No titration	
0.2515	7	8.80 7.80 1.00	$\frac{100(.05)(1.00)}{.2515} = 19.95$
0.1406	8	8.8 8.2 0.6	$\frac{100(.05)(0.6)}{0.1406} = 21.4$(high)
0.1402	9	23.65 22.75 0.90	$\frac{100(.05)(.90)}{0.1402} = 32.0$
0.0832	10	22.70 22.20 .50	$\frac{5(.5)}{.0832} = 15.0$
0.1278	11		

COMMENTS: (1) This was one of the earlier tests, and efficient technique and close control of titration was not established.

(2) Results of this run are somewhat higher than subsequent runs; but these results were plotted on graph.

ILLITE RUN #2
March 15, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration(mls.)	Base Exchange Capacity = 100 N (B-T) $\div$ W
0.0660	4	0.88 0.80 .08	$\frac{5(.08)}{.0660} = 6.0$
0.1068	5	1.04 0.91 0.13	$\frac{100(.05)(.13)}{0.1068} = 6.1$
0.1317	6	0.900 0.595 0.305	$\frac{100(.05)(.305)}{.1317} = 11.6$
0.0975	7	.55 .32 0.24	$\frac{100(.05)(.24)}{.0975} = 12.3$
0.1200	8	.93 .62 0.31	$\frac{0.31(5)}{0.1200} = 12.9$
0.0957	9	.62 .33 0.29	$\frac{5(.29)}{0.0957} = 15.11$
0.0950	10	0.29 0.00 0.29	$\frac{5(.29)}{.0950} = 15.25$
0.1038	11	5.00 4.70 0.30	$\frac{5(.30)}{.1038} = 14.0$

ILLITE RUN #3
April 3,1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration(mls.)	Base Exchange Capacity = 100 N B-T) ÷ W
0.1185	4	0.465 0.150 0.315	$\frac{5(.315)}{0.1185} = 13.3$
0.1090	5	0.740 0.470 0.270	$\frac{5(.270)}{0.1090} = 12.4$
0.1595	6	1.635 1.180 0.455	$\frac{5(.455)}{0.1595} = 14.2$
0.1178	7	0.185 0.145 0.330	$\frac{5(0.330)}{0.1178} = 14.0$
0.1007	8	1.180 0.720 0.460	$\frac{5(.460)}{0.1007} = 22.8$
.1004	9	1.650 1.180 0.470	$\frac{5(.470)}{0.1004} = 22.9$
0.1008	10	1.790 1.440 0.350	$\frac{5(.350)}{0.1008} = 17.4$
0.1010	11	1.090 1.790 0.300	$\frac{5(.300)}{0.1010} = 14.9$

ILLITE RUN #4
May 3, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration (Mls.)	Base Exchange Capacity = 100 N (B-T) ÷ W
0.1180	4	0.375 0.234 0.141	$\frac{5(.141)}{0.1180} = 6.0$
0.1090	5	0.460 0.325 0.135	$\frac{5(.135)}{0.1090} = 6.2$
0.0888	6	0.580 0.470 0.120	$\frac{5(.120)}{0.0888} = 6.75$
0.1385	7	0.800 0.580 0.220	$\frac{5(.220)}{0.1385} = 8.00$
0.1285	8	1.070 0.800 .270	$\frac{5(.270)}{0.1285} = 10.05$
0.1155	9	1.595 1.290 0.305	$\frac{5(.305)}{0.1155} = 13.2$
0.1420	10	1.290 1.140 0.150	$\frac{5(.150)}{0.1420} = 5.3$
0.1142	11	1,363 1.295 0.068	$\frac{5(.068)}{0.1142} = 3.0$

BENTONITE RUN #1
April 5, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05N H_2SO_4 used for Titration(mls.)	Base Exchange Capacity= 100 N (B-T) $\div$ W
0.1180	4	2.00 0.30 1.70	$\frac{5(1.70)}{0.1180} = 72.0$
0.0767	5	0.72 0.31 0.41	
0.1040	6	1.56 0.41 1.15	$\frac{5(1.15)}{0.104} = 56.0$
0.1204	7	1.61 0.01 1.60	$\frac{5(1.00)}{0.1204} = 66.5$
0.0962	8	1.55 0.15 1.40	$\frac{5(1.40)}{0.0962} = 72.8$
0.1015	9	3.14 1.49 1.65	$\frac{5(1.65)}{0.1015} = 81.3$
0.1180	10	2.02 0.63 1.39	$\frac{5(1.39)}{0.1180} = 59.0$
0.1140	11		

COMMENTS: 7 drops of Methyl Red used for indicator
Samples at pH 17 and 10 difficult to filter,
because sample peptizes.

BENTONITE RUN #2
April 19, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration(Mls.)	Base Exchange Capacity 100 N (B-T) ÷ W
0.1391	4	1.850 0.100 1.75	$\frac{5(1.75)}{0.1391} = 63.1$
.0848	5	1.125 0.435 0.690	$\frac{5(.690)}{0.0898} = 40.8$
.0780	6	1.925 1.125 0.800	$\frac{5(.800)}{.0780} = 51.5$
0.1045	7	1.770 0.600 1.170	$\frac{5(1.170)}{0.1045} = 56.1$
0.1050	8	2.600 0.440 2.160	$\frac{5(2.160)}{0.1050} = 103.0$
0.1000	9	1.950 0.420 1.530	$\frac{5(1.530)}{0.1000} = 76.7$
.0650	10	0.950 0.345 0.605	$\frac{5(0.605)}{.0650} = 46.5$
.0870	11	1.450 0.940 0.510	$\frac{5(.510)}{.0870} = 29.1$

BENTONITE RUN #3

May 5, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 H_2SO_4 used for titration(mls.)	Base Exchange Capacity= 100 N(B-T) ÷ W
0.125	7	3.2 1.0 2.2	$\frac{100(.05)2.2}{0.125} = 88.1$
Remarks:	Micro-burette would increase accuracy of titration measurements.		
0.0700	4	0.980 0.350 0.630	$\frac{5(.630)}{0.0700} = 45.0$
0.1156	5	2.090 0.980 1.110	$\frac{5(1.110)}{0.1156} = 48.0$
0.1243	6	2.000 0.458 1.515	$\frac{5(1.515)}{0.1243} = 60.5$
0.1025	7	1.562 0.375 1.187	$\frac{5(1.187)}{0.1025} = 58.0$
0.1078	8	2.890 1.562 1.328	$\frac{5(1.498}{0.1078} = 69.5$
0.1045	9	2.000 0.710 1.290	$\frac{5(1.290)}{1.045} = 62.0$
0.1107	10	1.440 0.310 1.130	$\frac{5(1.130)}{0.1107} = 51.0$
.0858	11	2.035 1.440 0.595	$\frac{5(.595)}{.0858} = 34.6$

MIXED SAMPLE*
April 10, 1951

Dry Wt. Sample (Gms.)	pH Amm. Acetate	.05 N H_2SO_4 used for Titration(mls.)	Base Exchange Capacity = 100 N (B-T) ÷ W
0.0877	9.1	1.660 1.065 0.595	$\frac{100(.05)(.595)}{.0872} = 34.0$
0.0968	9.1	1.380 0.780 0.600	$\frac{100(.05)(.60)}{.0968} = 31.0$
0.1080	9.1	0.780 0.130 0.650	$\frac{100(.05)(.65)}{0.1080} = 30.2$
0.1200	9.1	1.885 1.460 0.425	$\frac{100(.05)(.425)}{0.1200} = 20.2$
0.0765	9.1	0.790 0.385 0.405	$\frac{100(.05)(.405)}{0.0765} = 26.5$
0.1015	9.1	1.260 0.850 0.410	$\frac{100(.05)(.410)}{0.1015} = 20.2$
0.0968	9.1	1.680 1.270 0.410	$\frac{100(.05)(.410)}{0.0968} = 21.2$

*SAMPLE composed of equal parts by weight of Kaolin, Illite, and Bentonite.

DATA

Computed B.E. Value from Spectrograph

Kaolinite Oxide diff. in % treated and untreated

CaO	.103
TiO_2	.010
MgO	.010
K_2O	.060
Na_2O	.030

Ca $\quad .103 \times \frac{40}{56} \times \frac{2}{40} \times 1000 = 3.68$

Ti $\quad .01 \times \frac{48}{80} \times \frac{4}{48} \times 1000 = 0.50$

Mg $\quad .01 \times \frac{24}{40} \times \frac{2}{24} \times 1000 = 0.50$

K $\quad .06 \times \frac{78}{94} \times \frac{1}{39} \times 1000 = 1.27$

Na $\quad .03 \times \frac{46}{62} \times \frac{1}{23} \times 1000 = \underline{0.97}$

6.92 m.e./100g

Illite Oxide diff. in % content

CaO	.213
TiO_2	.125
MgO	.130
K_2O	.190
Na_2O	.021

Ca $\quad .213 \times \frac{1000}{28} = 7.62$

Ti $\quad .125 \times \frac{1000}{20} = 6.25$

Mg $\quad .130 \times \frac{1000}{20} = 6.50$

K $\quad .190 \times \frac{1000}{47} = 4.05$

Na $\quad .021 \times \frac{1000}{31} = \underline{0.68}$

25.10 m.e./100g

<u>Bentonite</u> Oxide diff . in % content

CaO	.090
TiO_2	.100
MgO	1.760
K_2O	0.040
Na_2O	0.100

Ca $.09 \times \frac{1000}{28} = 3.21$

Ti $.10 \times \frac{1000}{20} = 5.00$

Mg $0.76 \times \frac{1000}{20} = 38.00$

K $.04 \times \frac{1000}{47} = 0.85$

Na $.10 \times \frac{1000}{31} = \underline{3.23}$

50.29 m.e.100g

METHOD USED FOR COMPUTING RESULTS OF SPECTROGRAPHIC ANALYSIS

From the analysis curves, the concentration ratios

$$\frac{\%Al_2O_3}{\%SiO_2} \quad \frac{\%Fe_2O_3}{\%SiO_2}\text{, etc.} \quad \text{are obtained.}$$

To determine $\%SiO_2$:

$$\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3 + \%MgO + \%TiO_2 + \%CaO$$

$$+ \%K_2O + \%Na_2O + \%\text{Ignition loss} = 100$$

Solving

$$\%SiO_2 = \frac{100 - \%\text{ Ignition loss}}{1 + \frac{\%Al_2O_3}{\%SiO_2} + \frac{\%Fe_2O_3}{\%SiO_2} + \frac{\%MgO}{\%SiO_2} + \frac{\%TiO_2}{\%SiO_2} + \frac{\%CaO}{\%SiO_2} + \frac{\%K_2O}{\%SiO_2} + \frac{\%Na_2O}{\%SiO_2}}$$

To determine % of other constituents

Example $\%Al_2O_3$

$$\%Al_2O_3 = \%SiO_2 \times \frac{\%Al_2O_3}{\%SiO_2}$$

SAMPLE COMPUTATIONS

Example H-Bentonite

Concentration Ratios — Ignition loss = 9.34%

Fe_2O_3	.0247
Al_2O_3	.055
CaO	.00005
TiO_2	.00127
MgO	.0281
K_2O	.00346
Na_2O	.00494

$$\% \ SiO_2 = \frac{100 - 9.34}{1 + .0247 + .055 + .00005 + .00127 + .0281 + .00346 + .00494}$$

$$\% \ SiO_2 = \frac{90.66}{1.11752} = 81.0$$

$$\begin{aligned}
\% Fe_2O_3 &= 81.0 \times .0247 = 2.000 \\
\% Al_2O_3 &= 81.0 \times .055 = 4.450 \\
\% CaO &= 81.0 \times .00005 = 0.040 \\
\% TiO_2 &= 81.0 \times .00127 = 0.103 \\
\% MgO &= 81.0 \times .0281 = 2.280 \\
\% K_2O &= 81.0 \times .00346 = 0.280 \\
\% Na_2O &= 81.0 \times .00494 = \underline{0.400} \\
& \qquad\qquad\qquad\quad 9.553
\end{aligned}$$

check = 9.553 + 81.0 + 9.34 = 99.893%

METHOD OF CALCULATING BASE EXCHANGE

VALUE FROM SPECTROGRAPHIC ANALYSIS

B.E.V. = Base exchange value in m.e./100g

$$\text{Difference in \% Oxide Present} \times \frac{\text{Molecular Wt. of Element}}{\text{Molecular Wt. of Oxide}}$$

$$= \frac{\text{grams of element}}{\text{100 g of sample}}$$

$$\text{BEV} = \frac{\text{g Element}}{\text{100g sample}} \times \frac{\text{1equiv.wt.}}{\frac{\text{gram atom.wt.Element}}{\text{Valence of Element}}} \times \frac{\text{1000m.e.}}{\text{equiv.wt.}}$$

Sample Computation Bentonite

Oxide	Diff. in % Content
CaO	.090
TiO_2	.100
MgO	1.76
K_2O	0.04
Na_2O	0.10

Ca $.09 \times \frac{40}{56} \times \frac{2}{40} \times 1000 = 3.21$

Ti $.10 \times \frac{48}{80} \times \frac{4}{48} \times 1000 = 5.00$

Mg $1.76 \times \frac{24}{40} \times \frac{2}{24} \times 1000 = 38.00$

K $.04 \times \frac{78}{94} \times \frac{1}{39} \times 1000 = 0.85$

Na $.10 \times \frac{46}{62} \times \frac{1}{23} \times 1000 = 3.23$

50.29 m.e./100g

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